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STUDIES IN THERMOELECTRET AND
PHOTOELECTRET STATES OF
POLYMERIC MATERIAL
(Polyvinylacetate)

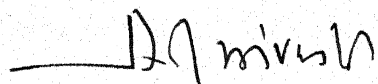
THESIS
SUBMITTED FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY
IN
PHYSICS

By
J. P. Srivastava
Deptt. of Physics, D. V. College, ORAI (U. P.)

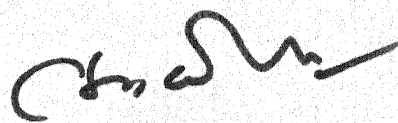
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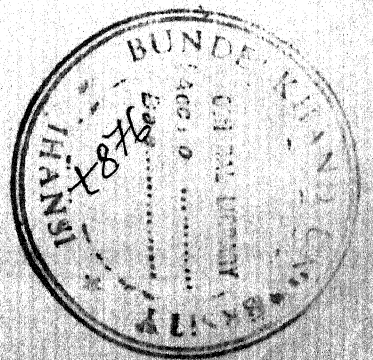
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Professor and Head of
Physics Department, University of Sagar,
Sagar



Principal
D. V. COLLEGE
ORAI [U. P.]



**Studies in Thermoelectret and Photoelectret
States of Polymeric Material**

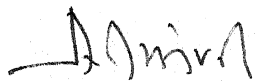
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LIST OF PUBLICATIONS

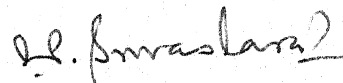
1. Thermally stimulated discharge currents from unpoled iodine doped polyvinylacetate, Japanese Journal of Applied Physics, Vol 20, 2439 (1981). (Attached at the end).
2. Thermally stimulated discharge currents from polyvinylacetate, Thin Solid Films, Switzerland. (Revised and resubmitted).
3. Electrode effect on photodepolarization currents from pure and iodine doped polyvinylacetate, Indian Journal of Pure and Applied Physics. (Revised and resubmitted).
4. Effect of iodine doping on photopolarization of polyvinylacetate, Journal of Polymer Science, (USA) (Submitted).

DECLARATION

I hereby declare that with the exception of the guidance received from my guide, this thesis is my own unaided work.



Supervisor
Dr. A.P. Srivastava
Professor of Physics
Sagar University
Sagar, M.P.



(J.P. Srivastava)

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(J.P. Srivastava)

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PREFACE

Polymers are known to be good electret forming materials. Polymer film electrets have several applications in modern solid state devices. Though vast literature on electret forming characteristics of polymers has poured in recent years, yet the mechanisms responsible for charge storage in polymers are ^{far} from being clear. Polyvinyl acetate (PVAc) is a polar polymer and comparatively less attention has been paid to understand its charge storage capability. It has been shown that electret forming characteristics of polymers can be greatly improved by doping them with suitable impurities. With this ^{vi} new, PVAc matrix has been doped with iodine. The thesis reports on electrical conduction, thermally stimulated discharge current, photodepolarization current and dielectric properties of pure and iodine doped PVAc films.

The thesis has been divided into eight different chapters. Chapter I introduces the problem and reviews briefly the previous works. It also deals with the choice of the polymer and the dopant. Experimental details are given in chapter II emphasising various techniques of film preparation, method of doping the polymer and the electrode assemblies used. Chapter III reports transient behaviour of current, electrode material and thickness dependences of current-voltage characteristics of PVAc and current-voltage-temperature characteristics of pure and iodine doped films. Thermally stimulated

discharge currents in PVAc films as a function of field, temperature, film thickness, electrode material, heating rate and iodine concentration are reported in chapter IV. Chapter V discusses photodepolarization currents released from pure and iodine doped PVAc photoelectrets by varying the field, time, polarity and electrode material. Dielectric properties of pure and iodine doped PVAc films in audio-frequency range are described in chapter VI. Chapter VII correlates the results of different studies while chapter VIII presents the summary with concluding remark.

CHAPTER I

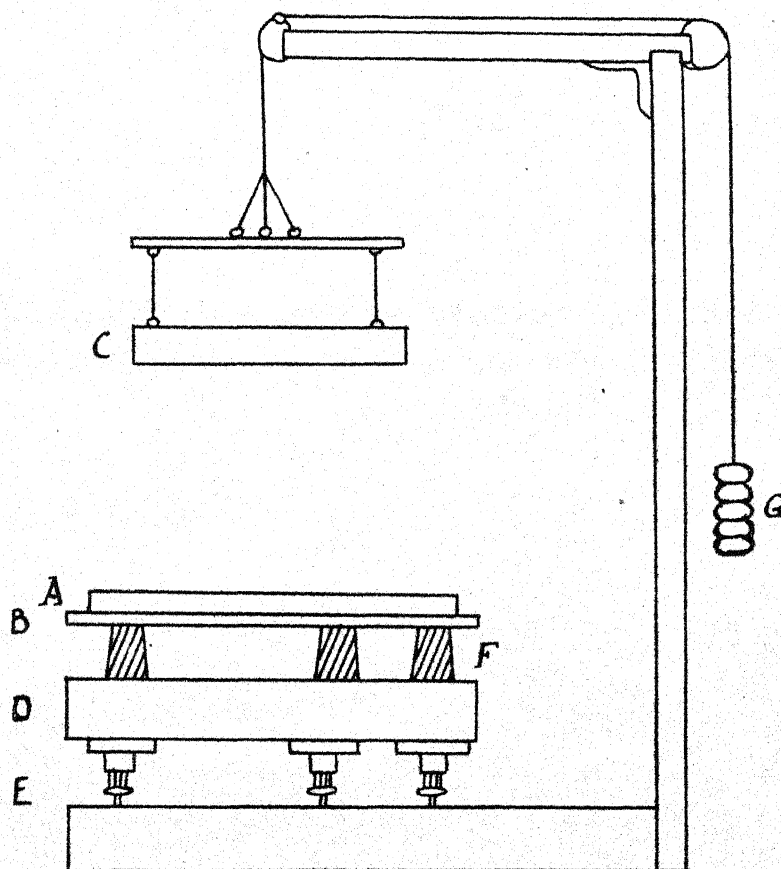
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INTRODUCTION

1.1 Definition and types of electret

An electret is understood as a body composed of a dielectric, which preserves its polarization for a long time after the external electric field that has produced this polarization is removed, and which sets up an electrostatic field in the surrounding space.

The word 'electret' is formed by analogy with the word 'magnet'. An electret establishes an electric field for a long time in the same way as a permanent magnet sets up a continuous magnetic field. The existence of electrets was surmised by the Russian academician F. Epinus and later by the English physicist O. Heaviside¹ who introduced in 1896 the term 'electret' and studied some theoretical problems related to electrets. But it was only in 1921 that the Japanese researcher M. Eguchi^{2,3} actually received and investigated the electrets. After this, the electrets have become the object of numerous experimental and theoretical studies and found an increasingly wider practical application. Figure 1.1 illustrates the installation designed by Eguchi in which the first electrets have been obtained. A round metal bath A with an inlet B placed on insulators F and support D is adjusted strictly horizontally with the aid of screws E. The bath is filled with a molten dielectric (a mixture of wax and resin) after which electrode C suspended from a thread with counter weight G is



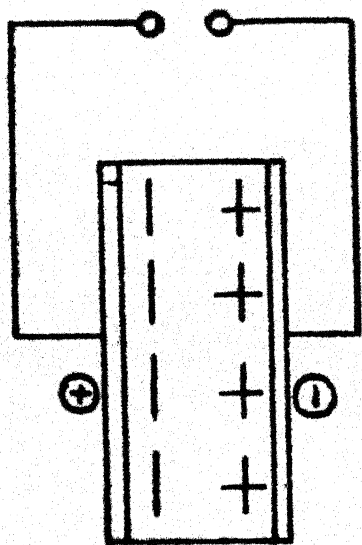
*A-METAL BATH B-INLET C-ELECTRODE
D-SUPPORT E-SCREWS F-INSULATORS G-COUNTER WEIGHT
EGUCHI'S INSTALLATION FOR OBTAINING THERMOELECTRET'S*

Fig-1.1

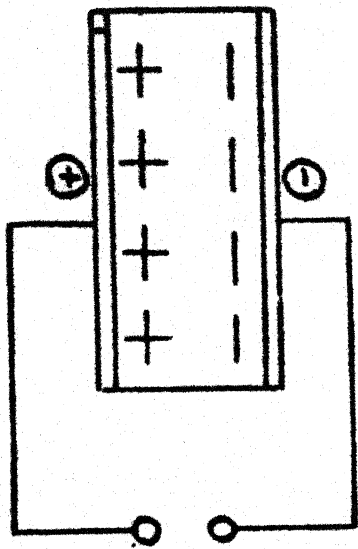
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let down until it touches the surface of the dielectric, and a direct-current voltage is applied between electrodes A and C. This voltage is maintained until the molten dielectric cools down and solidifies in the electric field. Such a dielectric becomes an electret, the opposite surfaces of the disk have unlike charges which can persist for years, especially if the electret is shorted. (Similar to a magnet with the poles short-circuited through a ferromagnet). If the outer layers of the dielectric are cut off the charge of the electret will not be changed, while two electrets are obtained when the original electret is cut along the neutral plane (in the same way as when a magnet is cut in two parts). If an electret is moistened or intensely irradiated by X-rays most of the charge is lost, but after drying or cessation of irradiation the charge is restored. A completely molten electret will be fully discharged.

It has been found later that when a heated dielectric is cooled in an electric field, electrets (so called thermoelectrets) can be obtained from various dielectrics - both organic (polymethylmethacrylate, polytetrafluoroethylene, polyethyleneterephthalate, ebonite, ceresin, naphthalene, bee wax etc.) and inorganic, as has been demonstrated for the first time by Gubkin and Skanavi⁴ (titanates of various metals - barium, magnesium, zinc, calcium, etc., steatite, sulphur and others). The intensity of polarizing electric field appreciably affects the properties of an electret, when the electric field



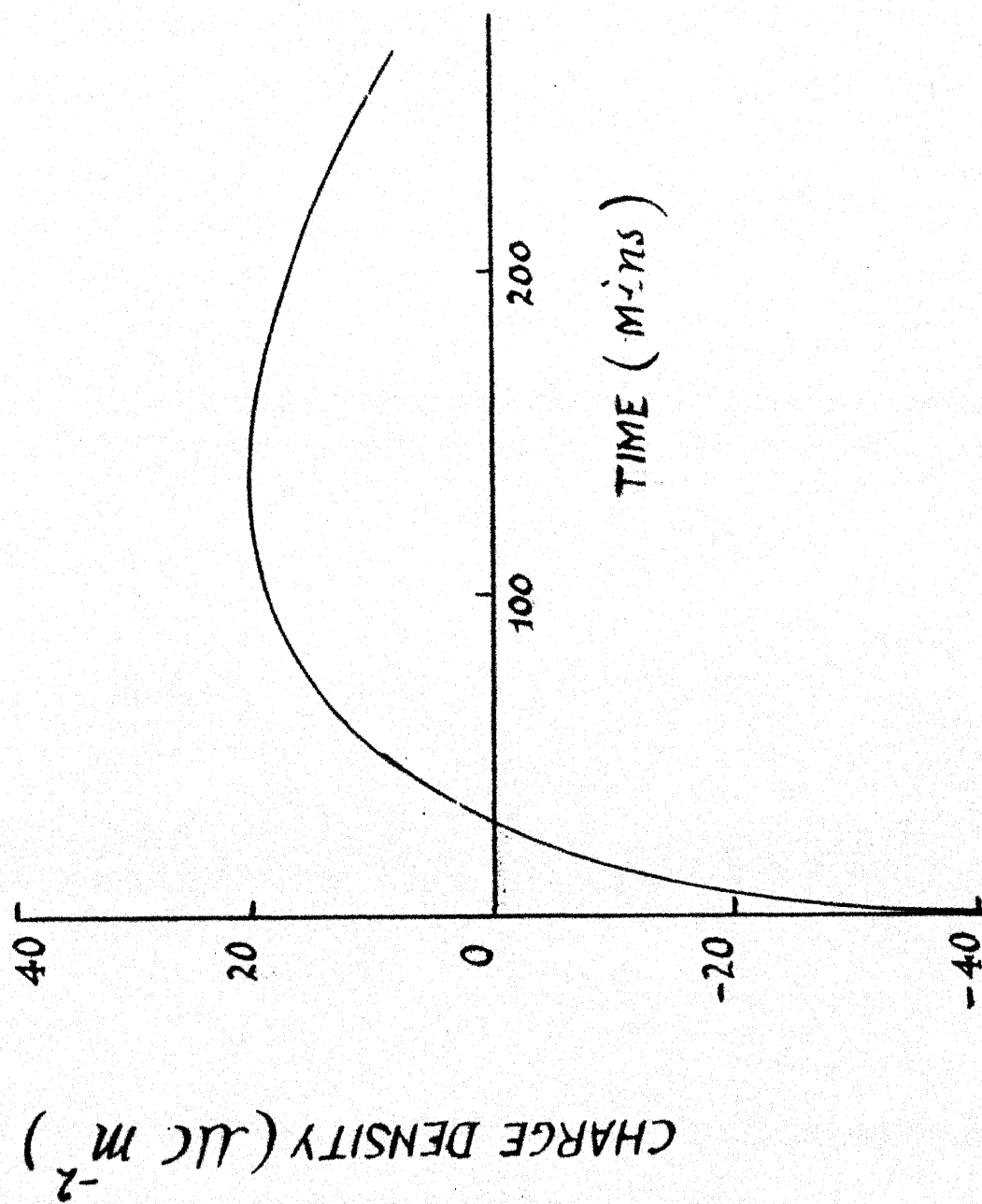
HETEROCHARGE



HOMOCHARGE

HETEROCHARGE AND HOMOCHARGE OF ELECTRETS

Fig. 1.2



CHARGE DENSITY OF AN ELECTRET MADE OF CARNAUBA WAX
VERSUS TIME ELAPSED AFTER POLARIZATION OF THE ELECTRET

Fig - 1.3

is small (approximately upto 10 kV cm^{-1}) the obtained electret possesses charges opposite to the polarity of the polarizing voltage (fig 1.2, on the left). If the electric field is greater than 10 kV cm^{-1} the electret receives charges of the same sign as the electrodes with which the surfaces of the electret were in contact during polarization (fig 1.2, on the right). The charges of the first type are known as heterocharges and of the second type as homocharges⁵. The stability of these types of charges can be different⁶. An example is illustrated in fig 1.3 which shows that in this case after a comparatively rapid drop of the heterocharge, a homocharge is set up which is reduced rather slowly.

If an electret is properly manufactured the charges produced on its sides may have a surface density upto 10^{-9} c/cm^2 ⁷. This density of charges corresponds to the intensity of the field near the surface of the electret upto 10 kV cm^{-1} , which approaches the magnitude of the electric strength of the air. An electret obtained in an atmosphere of increased pressure may have a surface density of charges upto $5 \times 10^{-9} \text{ c/cm}^2$ ⁸.

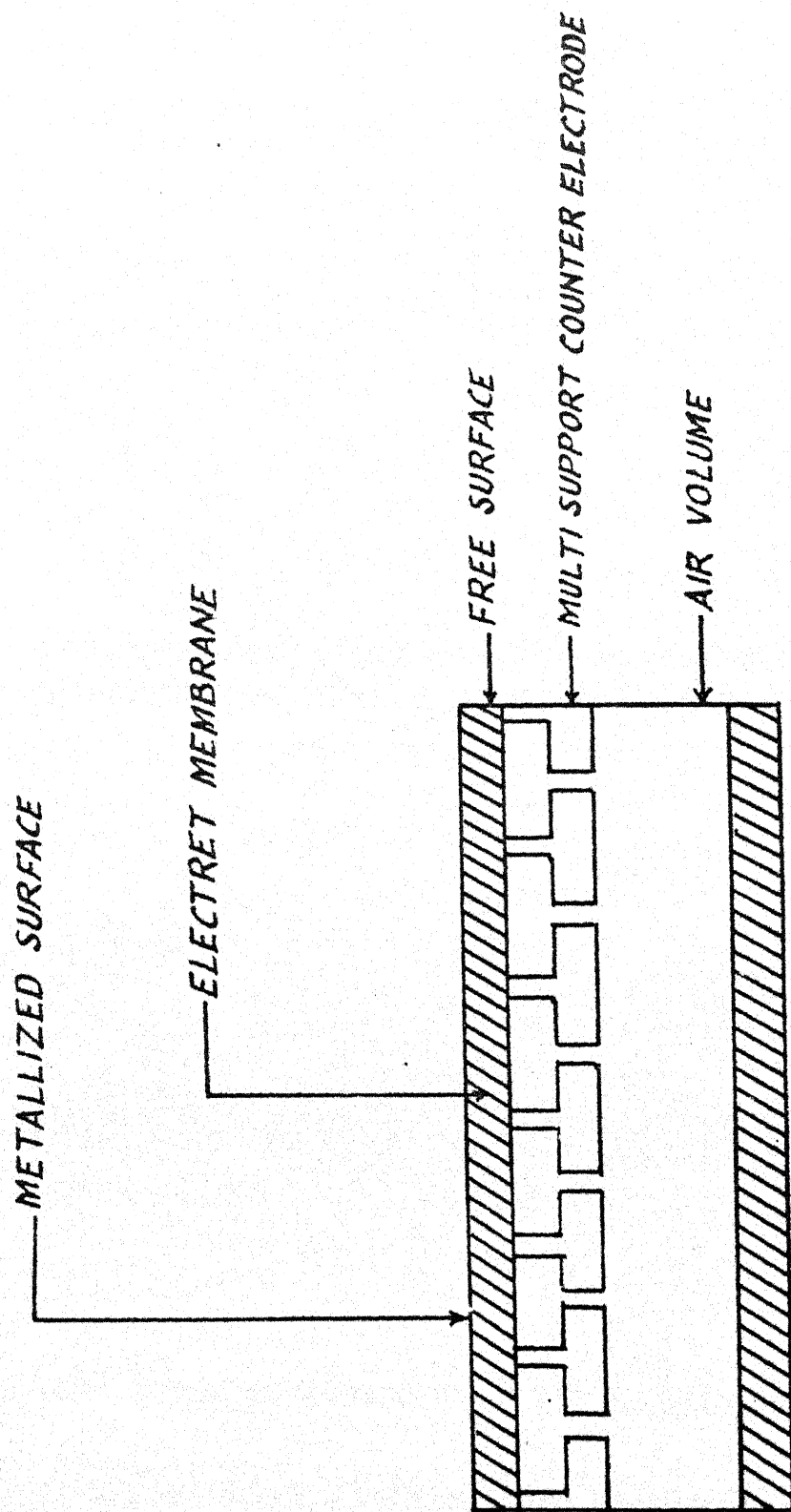
The method of manufacture of electrets (thermo-electrets) described above and employed under an increased temperature is not the only one. In 1937, Nadjakov⁹ of Bulgaria devised a new type of electret-photoelectret. Such electrets are made of photoconductive (i.e. acquiring a higher electrical conductivity with illumination) dielectric (sulphur, anthracene etc.). To make a photoelectret, a dielectric placed into a

strong electric field is illuminated after which the field is taken off. Photoelectrets possess a charge (usually a hetero-charge) which can be preserved for a long time if the photoelectret is kept in darkness (when exposed to light, the charge disappears).

Electroelectrets are obtained under the action of an electric field without heating a dielectric, radioelectrets are produced by radio-active radiation and mechanoelectrets, by a mechanical effect, i.e., deformation or friction of a dielectric. There are other data (not fully confirmed as yet) about other types of electrets⁴. Under an ionizing irradiation, x-rays for example, some dielectrics become pseudo electrets obtained without the application of voltage. Magneto-electrets, first discovered by C. Bhatnagar of India, form when a heated metal (polymethylmethacrylate, for examples) is acted upon by a strong permanent magnetic field with a subsequent cooling also in a magnetic field.

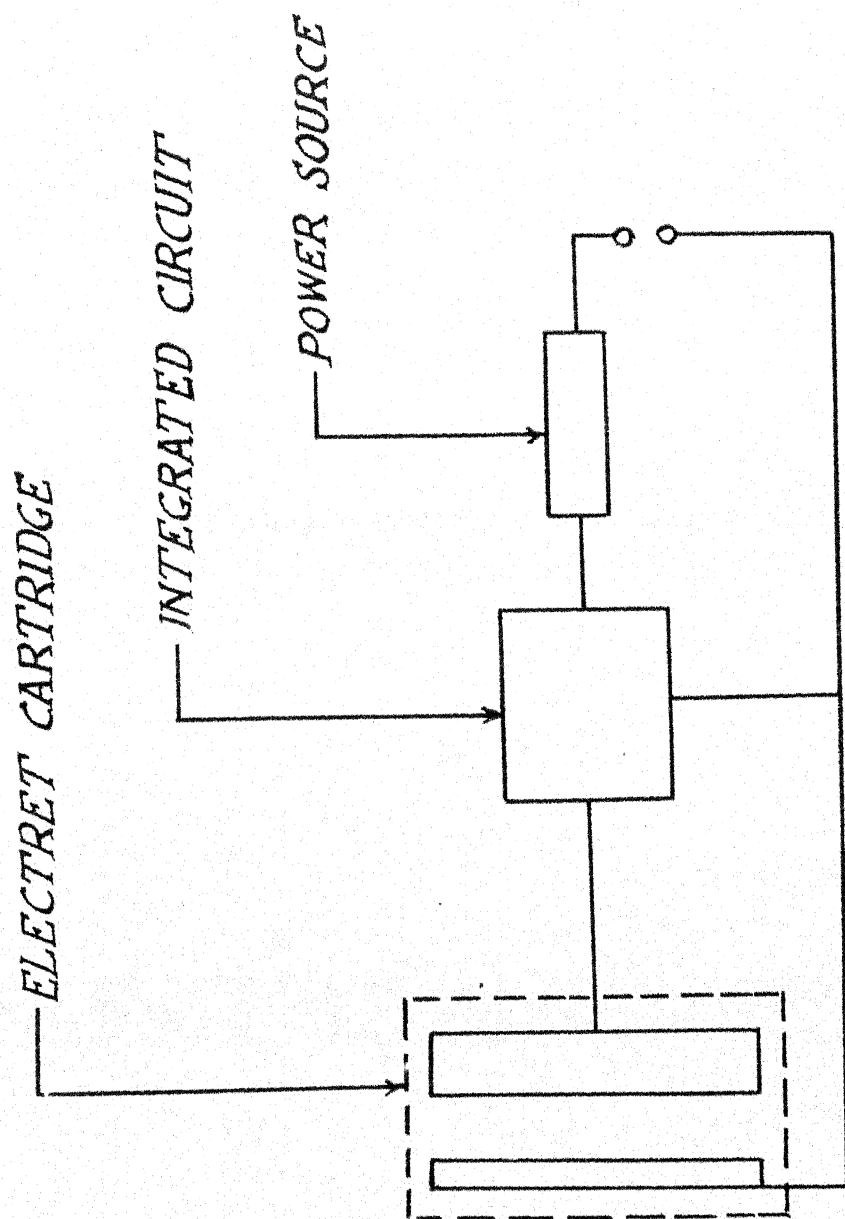
1.2 Application of electret

Many proposals have been made for the use of electrets in electrostatic measuring instruments, electrostatic voltage generators¹⁰, piezoelectric devices, air filters, radiation dosimeters, electrophotography, prosthetic devices, memory devices and microphones¹¹. Electret microphones are commercially produced by the Sony Corporation in Japan. Basic research and development work has also been done at Bell



ELECTRET MICROPHONE

Fig-1.4



BLOCK DIAGRAM OF CIRCUIT USED IN ELECTRET MICROPHONE

Fig - 1.5

Research Laboratories in USA and Northern Electric, Canada and elsewhere.

The performance of the electret microphone as a high fidelity instrument is as good or better than that of the condenser microphone. It does not need the separate battery of about 140 V necessary to energize the latter. The small dimensions of the microphone cartridge and use of integrated circuitry facilitate miniaturization of the equipment. The low internal and mechanical noise level enables the microphone to be incorporated in the chassis of tape-recorders.

An electret microphone is shown schematically in fig 1.4. The sound-sensitive element is an externally metallized and grounded plastic electret membrane about 0.01 mm thick. The oscillations of the electric field paralleling the vibrations of the membrane induce signals on the back-plate which are amplified. The same system, operating in the reverse sense, functions as a loudspeaker. Figure 1.5 shows a block diagram.

Attempts have been made to use electrified polymers as blood-compatible materials in prosthetic devices. The blood components which are likely to cause clotting in contact with the plastic tubing used to replace arteries, in particular the platelets, are negatively charged. For platelets charge densities of about 5×10^{12} electronic charges/cm² have been reported, similar values can be obtained with electrets. A negative surface charge of the inner walls of the tubes which are used as inserts and are in contact with the blood flow should

prevent or at least reduce platelet deposition and thus help to prevent clotting.

1.3 Theories of thermoelectret

Various theories have been put forward to explain the formation and behaviour of electrets. Since the thermoelectrets were discovered earlier, more literature is available on them as compared to others. All the theories were framed to explain three important facts concerning the thermoelectret.

- (i) The mechanism of electret formation which gives rise to persistent internal polarization.
- (ii) Longer life time of electrets.
- (iii) Phenomenon of charge reversal.

The important contributions are due to Adams¹², Gemant¹³, Thiessen, Winkel and Herrman¹⁴, Swann¹⁵, Baldus¹⁶, Gerson and Rohrbaugh¹⁷, Wiseman and Feaster¹⁸, Handerek and Piech¹⁹. Perlman and Meunier²⁰ explained quantitatively the charge decay of unshielded dielectric of finite resistivity and concluded that the internal field is the main decay agent governing both polarization growth and real surface charge decay which together account for the decay of net surface charge. There is no net local charge within the volume of the dielectric. The real surface charge decays only by ohmic conduction through the volume of the dielectric.

Gross²¹ proposed that the heterocharge is formed

by all the processes of charge absorption in a dielectric and the homocharge is due to the breakdown of the dielectric-electrode interface. The gradual decay of internal polarization with the retention of surface charge received by the thermoelectret from the electrode, is responsible for conversion of heterocharge into homocharge. His investigations showed that the surface charge of the thermoelectret is in general equal to the difference between the intrinsic heterocharge and intrinsic homocharge. The charge reversal from hetero to homo is due to a more rapid decay of the intrinsic heterocharge compared with the decay of the intrinsic homocharge. At low temperature when the intrinsic homocharge varies slowly with time, the conversion of charge may not be observed.

Recently Gross²² described the polarization picture of an electret after studying the volume distribution of charge by a modified sectioning technique. He suggested that the central bulk portion of the substance is separated from the surface near the electrode by a thin layer of a different dielectric constant. The heterocharge which resides in the central section is associated with a persistent volume polarization and space charge polarization. The homocharge is produced due to surface conduction or breakdown of dielectric-electrode interface. If the contact is blocking, homocharge will decay by conduction through bulk of the dielectric and if the contact is good, the homocharge will flow by conduction through dielectric-electrode interface.

1.4 Theories of photoelectret

Phenomenological theories of photoelectret have been proposed by Kallmann and Coworkers²³⁻²⁸, Fridkin and Zheludev²⁹⁻³², Chetkarov³³ and Adirovich³⁴. The conclusions of these theories agree qualitatively with some of the experimental observations, although the approach towards the mechanism of polarization is different. Tartakovskii and Rekhalova³⁵ and Kalabukhov and Fischelev³⁶ proposed that illumination produces transitions of electrons from the valence band to the conduction band, where they move under the influence of applied electric field. The electrons then leave the conduction band and are trapped at localized levels lying below the bottom of the conduction band. Freeman, Kallmann and Silver²³ suggested that an electric polarization is due to an inhomogeneous charge distribution brought about by an external field acting on free charge carriers. Internal polarization effects are described in terms of the 'frozen in' charge distributions. The build up of polarization occurs during external field application while the photoconductivity is in a state of excitation. This separation persists after excitation and field removal because of trapping processes. For these frozen-in charge distribution, static models have been developed. Experiments²⁸ show that two fundamentally different internal charge distributions can develop barrier and bulk polarization. Barrier polarization is produced when surface resistive layers interfere strongly with charge transport through the sample. The free positive and

negative charge carriers accumulate near the electrodes because of high resistive layers at the photo conductor-electrode interfaces. If these two resistive layers are of the same magnitude, the barrier polarization leaves the sample electrically neutral. Furthermore, it is not necessary that the sample be uniformly excited during polarization. In bulk polarization, the more mobile carriers are atleast partially removed from the sample with the less mobile carriers remaining in a fairly uniform distribution over the bulk of the sample. According to Frickin et al³⁰, the photo polarization state produced by the application of field and light, is based on the scheme of electronic energy levels and the investigation of space charge in photo-conduction provide a basis for understanding photoelectret mechanism.

It may, however, be pointed out that a theory which successfully explains the behaviour of thermoelectrets, might prove quite inadequate to explain that of others. Although a number of theories have been suggested by various workers, yet none of them is completely satisfactory. Thus electret state of materials provides a wide and rewarding area of research.

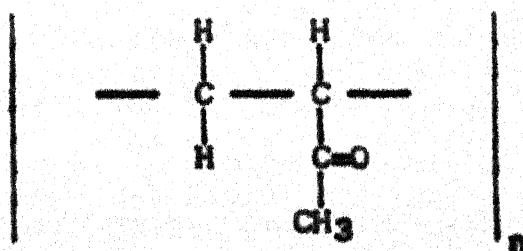
1.5 Material and the form of samples

Organic insulating materials^{37,38} have been the subject of considerable interest due to their wide applications in a number of devices. In recent years, the studies of these

materials in film form³⁹⁻⁴⁵ have attracted the attention of investigators due to their application in microelectronics and as electrets in a number of electrical devices. Due to their small size, thin specimens are preferred to the crystals of bulk material. The thin samples have still wider range of application as compared to bulk organic crystals.

Several techniques are available to form the films of organic materials⁴⁶⁻⁴⁹. Among them are thermal evaporation⁵⁰, sputtering techniques⁵¹ or chemical deposition methods⁵². The films formed by thermal evaporation result in degradation of materials, such films also suffer from the presence of pinholes and voids. The problem of pinholes can be controlled in films prepared by sputtering or chemical deposition. However, materials suffer from degradation in sputtering technique. The problem of degradation of the material can be overcome in case of polymeric organic materials^{53,54}.

Polyvinylacetate (PVAc) has been chosen for the present investigation. It has the following chemical structure.



n = the number of monomer junctions.

PVAc is an amorphous polymer. Its supermolecular

organization is explained in terms of cluster structure. By Clusters Ubbelode⁵⁵ means the regions (domains) that have a denser packing of the molecules (or their parts) and a more ordered arrangement of them in comparison with the main looser and unordered mass of a substance. It is natural that the density of a cluster should be some what greater than the average density of a substance. At the same time clusters are less ordered and less densely packed domains than crystallites. Clusters exist that in definite conditions are capable of having a more ordered arrangement of their molecules, i.e. are capable of crystallization. On the otherhand, the existence of clusters that in principle do not crystallize is also possible. Since regular packing of the particles in three dimensions in this case is absent, then when cooled from a melt, anti-crystalline clusters can not continue to grow unlimitedly without the appearance of voids or dislocations. If the model proposed by Ubbelode⁵⁵ is applied to polymers, it can be assumed that in addition to crystalline regions, a polymer may also have crystallizing and non-crystallizing clusters. In this connection a polymer may be considered as a complex of separate domains forming different parts (by volume) of the total volume of a polymer and organized in different ways. From that stand point, PVAc can be considered as a complex of different kinds of non-crystallizing clusters among less ordered and looser regions.

The glass transition temperature is the most

important characteristic temperature of amorphous polymers. The concept of the glass transition temperature of polymers was introduced by Ueberreiter^{56,57}. There are different definitions of this temperature, two of which are in the greatest favour and are the most correct. By the glass transition temperature T_g is meant the temperature at which the viscosity of a polymer is 10^{13} poise⁵⁸. On the other hand, it is interpreted as the temperature below which segmental motion of the polymer molecules is frozen. There are many experimental methods for determining T_g . The most dependable one is its determination according to the temperature dependence of the specific volume on condition that the sample under study is subjected to thermostatic control for a sufficient time at each temperature point at which measurements are made. Acoustic methods are successfully used for determining the glass transition temperature⁶¹⁻⁶³. It is the most correct to determine the glass transition temperature according to the change in the temperature coefficient of the velocity of sound. In the glassy state with an unchanging nature of the molecular mobility, the velocity of sound depends linearly on the temperature. Above T_g , when unfreezing of segmental mobility of the micro-Brownian type begins, the temperature coefficient of the velocity of sound sharply changes. For PVAc, the velocity of sound changes most greatly at 40°C ⁶⁴. According to the data of dilatometric measurements, the glass transition temperature is equal to 30°C ⁶⁵. Wada and his Collaborators⁶⁶, using the

temperature dependence of the specific volume, found temperature transition at 35°C in PVAc. This shows that the glass transition temperature of PVAc lies in between 30° - 40°C.

1.6 Dopant material

One way of modifying polymers used to improve their properties is addition of impurities. Plasticizers are introduced into the polymers to decrease the effectiveness of inter-molecular (interchain) interaction⁶⁷. The microscopic effect of plasticizing usually manifests itself in a reduction of the glass transition temperature. Both low and high molecular substances are used as plasticizers. The plasticizing action depends on the chemical structure, size and shape of the plasticizer molecules⁶⁸. Gibbs and Marzio⁶⁹ showed that the effectiveness of the plasticizer depends, to a considerable extent, on the conformation set of its molecules. Plasticizers whose molecules can take on a greater number of conformations lower the glass transition temperature of a polymer to a great extent.

Certain applications of polymer films in solid state devices have necessitated increasing of their electrical conductivity. Several workers have reported increase in conductivity of polymers due to doping of them with several impurities. Polybutadiene has been doped with chloranil, 2-3 dichloro-5-6 dicyanobenzoquinone and tetracyanoethylene and an increase in conductivity and carrier mobility has been

observed⁷⁰. Low and high density polyethylenes have been doped with halogens and the largest increase in conductivity has been observed due to incorporation of iodine⁷¹. Recently polystyrene has been doped with acrylic acid⁷², chloranil⁷³, copperphthalocyanine⁷⁴, iodine⁷⁵, pyrene⁷⁶, ferrocene and anthracene⁷⁷ and a marked increase in conductivity of the polymer has been observed. These results show that the conductivity of polymers can be greatly affected by doping them with suitable impurities. Both inorganic^{78,79} and organic impurities⁷¹⁻⁷⁴ can be used to modify the electrical conductivity of polymers. Inorganic impurities have more profound effects than organic impurities. Halogens are known to form polymer-halogen complexes⁸⁰ with rigid matrices. Iodine is an strong electron acceptor type impurity and can affect greatly the conductivity of polymers. For the present work, iodine has been chosen as the material to be incorporated in PVAc.

1.7 Methods of investigation

The knowledge of electrical conduction is essential in order to understand the electret forming characteristics of the material. The bulk properties of the electret are investigated most directly by the sectioning technique¹¹. But planning the surface of a polarized dielectric is a drastic operation. It generates new surface charges by triboelectric and breakdown effects which falsify the results of surface charge measurements made with the dissectible capacitor⁸¹. Preferable is the

measurement of thermally stimulated currents⁸²⁻⁸⁶. Photoelectret state in the material can be investigated by measuring the photodepolarization current⁸⁷⁻⁹⁰. There is a definite co-relation between electrical conductivity and dielectric properties of the material⁹¹⁻⁹⁵. Therefore the work reports on electrical conduction, thermally stimulated current, photodepolarization current and dielectric properties of pure and iodine doped PVAc films.

CHAPTER II

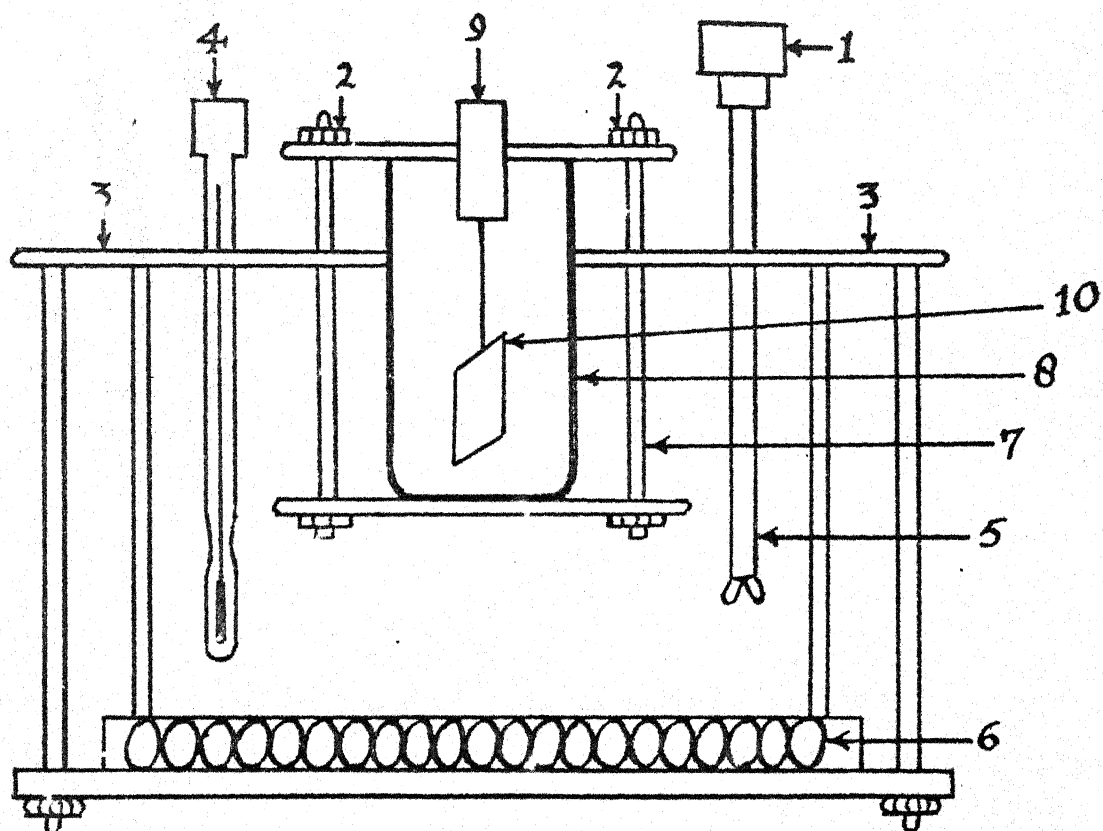
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EXPERIMENTAL DETAILS

2.1 Film preparation techniques

Materials can be casted into films by thermal evaporation⁹⁶, sputtering⁹⁷ and chemical deposition methods⁹⁸. In thermal evaporation, solid materials vaporise when heated to sufficiently high temperature. The condensation of the vapour on to a cooler substrate yields films. Evaporation can be carried out by flash, arc, and laser or by resistive, exploding wire, RF and electron bombardment heating. The ejection of atoms from the surface of a material by bombardment with energetic particles is called sputtering. If ejection is due to positive ion bombardment, it is referred to as cathodic sputtering. The sputtered atoms can be condensed on a substrate to form a film. Because of the high pressure of gas used and high sensitivity to contamination in commonly used glow discharge sputtering, the technique has generally been termed dirty. Sputtering can be achieved by low pressure, RF, ion beam and reactive sputtering. Electro or electroless deposition and anodic oxidation are chemical methods to deposit the films. In chemical vapour deposition technique, a volatile compound of the substance which is to be deposited, is vapourised. The vapour is thermally decomposed or reacted with other gases, vapours or liquids at the substrate to yield non-volatile reaction products which deposit atomistically on the substrate. Technology of film preparation has been reviewed by Chopra³⁰.

The irradiation technique for the preparation of polymer films is a high energy technique. Similarly RF sputtering of polymers is also a high energy process. In these high energy processes the cross linking of the polymer chains is highly probable. The films so formed show high dielectric losses and degradation with time. These films are, therefore, not suitable for practical applications. Films of polyvinyl chloride-acetate co-polymer⁹⁹ have been prepared by spreading cyclohexanone solution of the polymer over a water surface. Spivack¹⁰⁰ has prepared parylene (the generic name of a family of polymers based on poly-p-xylylene) films by using the vapour phase deposition process which has been described by Gorham¹⁰¹. The films thus formed have excellent mechanical, physical, electrical and barrier properties. They are virtually inert to most acids and bases and are insoluble in most organic solvents below 170°C. The isothermal immersion technique^{102,103} on the other hand, appears to be simple and powerful technique for obtaining durable and useful polymer films. Isothermal immersion technique has been used by several workers^{104,105} to prepare polymer films. In this method, the growth of the molecular chains on the substrate is predominantly lateral. The molecular chains or the clusters of the chains absorbed on the substrate attain a definite equilibrium size. These clusters do not significantly increase in size as the equilibrium thickness of the film increases but their number increases. The clusters tend to deform in one particular direction and the extent of deformation



1. MOTOR, 2-SUBSTRATE HOLDER ASSEMBLY SUPPORT
 3. OIL BATH COVER, 4-THERMOMETER, 5-STIRRER
 6. HEATING COIL, 7-POLYMER SOLUTION VESSEL SUPPORT
 8. SOLUTION CONTAINER, 9-SUBSTRATE HOLDER, 10-SUBSTRATE

ISOTHERMAL IMMERSION APPARATUS

Fig- 2.1

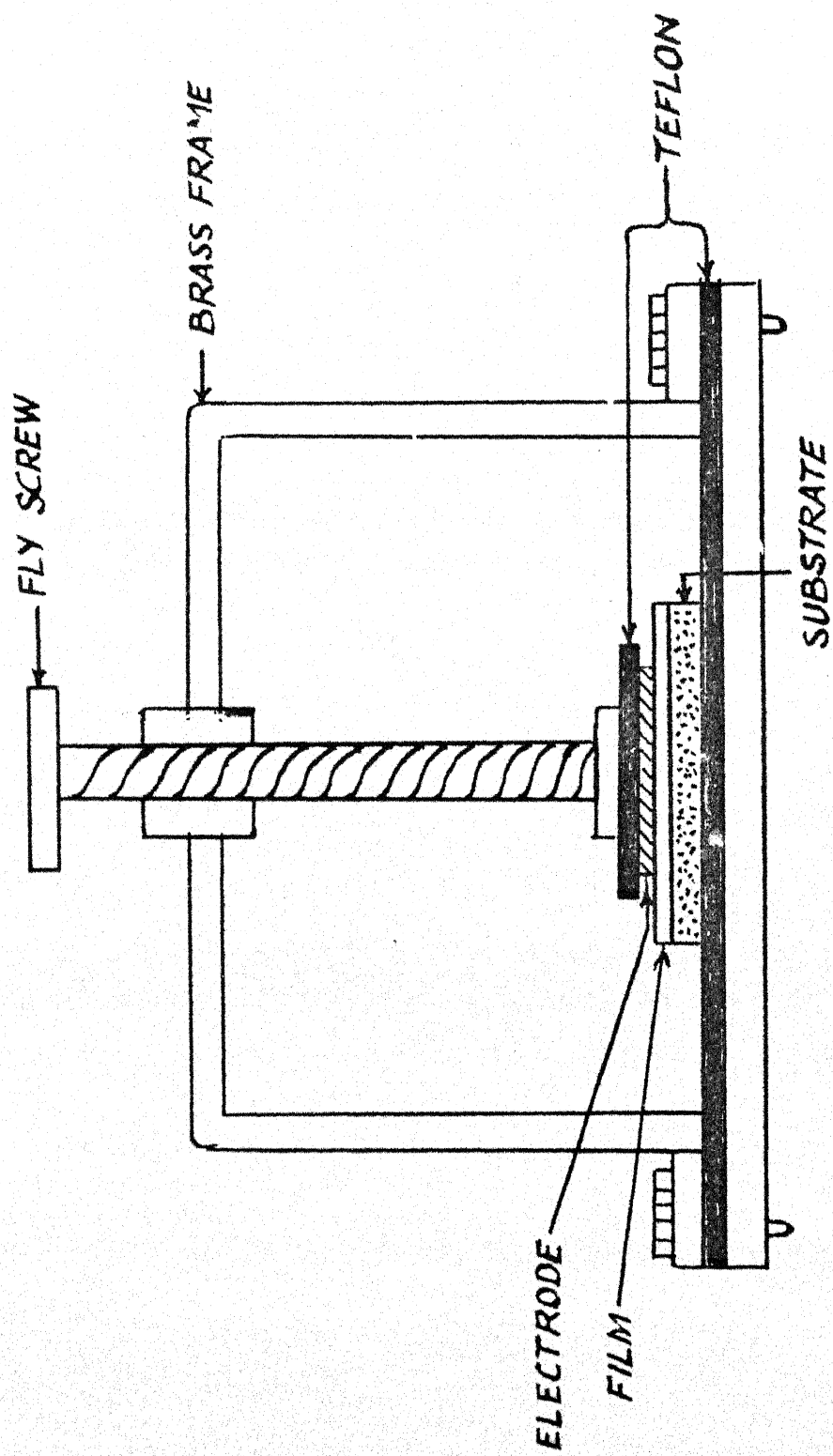
increases as the equilibrium film thickness increases. The clusters of the molecular chains have a preferred direction of orientation. Films of higher equilibrium thickness have more of amorphous areas surrounding the crystalline area.

It is clear from what has been stated above that the growth of films from solution occurs by adsorption controlled nucleation of molecular chains on the substrate and the further growth occurs by the attachment of more chains on the already adsorbed chains forming a cluster of chains. The adsorbed chains and subsequently the cluster of chains adjust themselves laterally on the substrate.

2.2 Preparation of PVAc films

PVAc from BDH chemicals, Poole (England) was used in the work. 5 gm of PVAc was dissolved in 10 ml of cyclohexanone. Aluminium substrates were used in the work. Al foils were cleaned by rubbing with cotton and then by keeping them immersed in benzene. The cleaned foils were stored in pure alcohol. Isothermal solution immersion growth technique of preparing the films involves isothermal immersion of the substrate into the polymer solution held at a particular temperature for certain time. The apparatus used to prepare the films is shown diagrammatically in fig 2.1.

PVAc solution was immersed in the oil bath. The temperature of the oil bath was kept constant at 40°C. The substrate was held in the constant temperature bath. After



ELECTRODE ASSEMBLY

Fig-2.2

bringing the solution and the substrate at 40°C, the substrate was immersed in the solution for 10 mins. The films were dried by keeping them within the thermostat at 40°C for more than 48 hrs.

2.3 Evaluation of film thickness

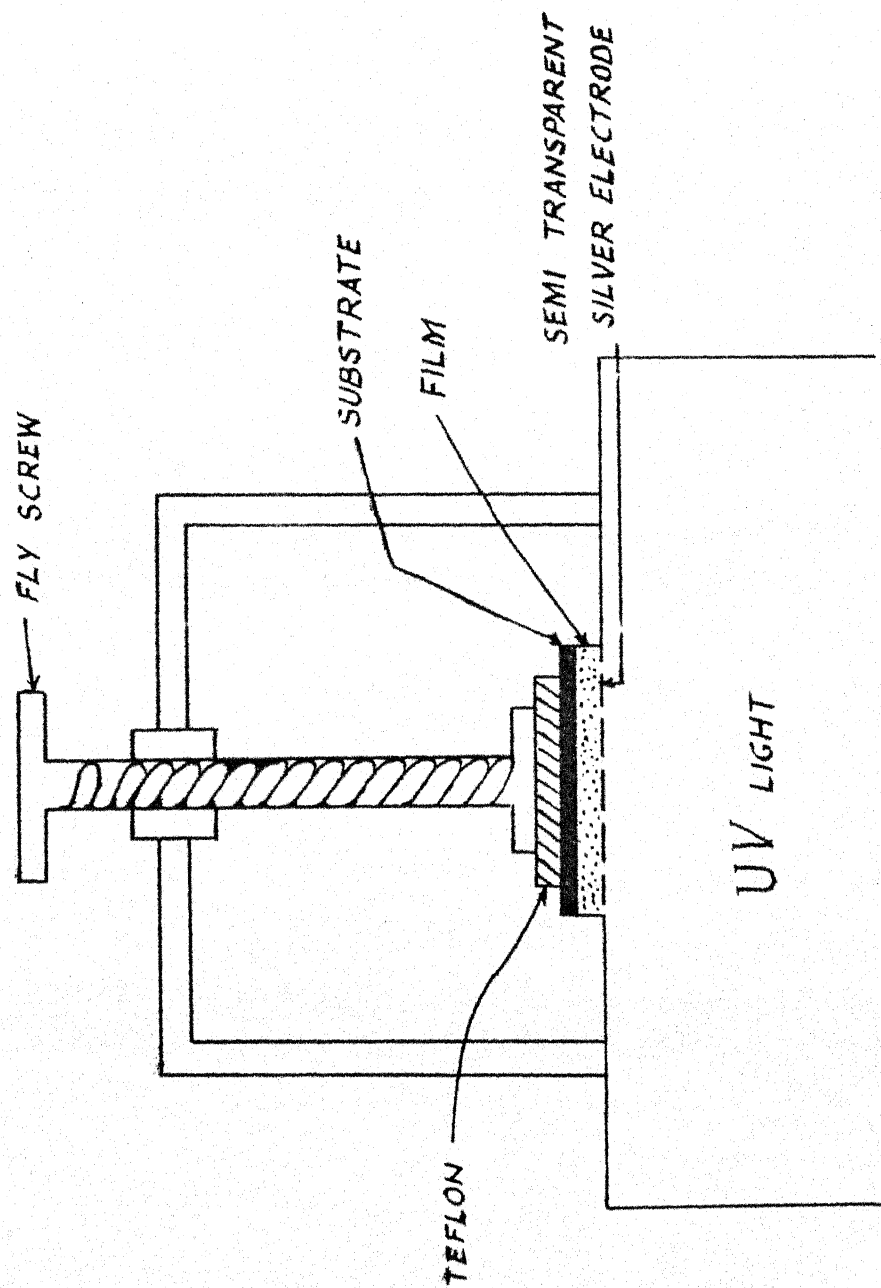
The thickness of the film was extrapolated by measuring its capacitance at 10 KHz and taking the permittivity value equal to 3.

2.4 Doping procedure

To dope the polymer iodine was dissolved in cyclohexanone to have the desired concentration and then the polymer was added into iodine solution to prepare the polymer solution. The doped films were prepared just like the undoped films. For electrode variation, PVAc films on Pb, Cu, Sn and Mo substrates were also prepared.

2.5 Electrode assembly

A pressed on electrode assembly was used in the investigation. It is diagrammatically shown in fig 2.2. The film alongwith the substrate was kept on the bottom teflon sheet so that the substrate contacted with the teflon. An Al electrode of 1 cm² in area surrounded with the guard ring to avoid the surface effects was pressed on to the film with the help of the flyscrew. The contact of the flyscrew with the electrode was



ASSEMBLY FOR PHOTO EXPERIMENT

Fig 2.3

insulated with a teflon disk. The substrate acted as another electrode.

2.6 Assembly for photo experiment

Assembly used in photo-polarization and depolarization experiments is schemetically shown in fig 2.3. UV light of wavelength 1518 \AA from a 15 watt — lamp was incident on the film through a semi-transparent silver electrode. The substrate acted as the other electrode.

2.7 Role of air in the present experimental set up

For fundamental studies vacuum deposited electrodes are preferable. However, in the present investigation pressed on electrodes have been used. In case of pressed on electrodes the contact between the electrodes and the polymer is imperfect and there are air spaces between them, in which at high field strengths townsend breakdowns will occur, so that ions or electrons from the air are injected into the polymer. The homo-charging by breakdown of the air is deliberately intensified in the manufacture of electrets. This development is logical, because the deposition of homocharges from the air is a much faster process than the heterocharging by dipole orientation and space charge motion within the polymer.

2.8 Measuring instruments

Currents were measured with EA 815 electrometer

which was carefully shielded and grounded so as to avoid ground loops or extraneous electrical noise. Temperature was measured with a precalibrated copper-constantan thermocouple. The thermoelectric emf. generated was noted with a d.c. micro-voltmeter. Capacitances and losses were measured with a LCR systronics bridge incorporating an audiofrequency oscillator (from Toshniwal).

2.9 Electrical conductivity measurement

Electrical conductivity of dielectrics is generally investigated either by heating the sample over a temperature range at a constant rate and keeping the applied voltage constant or by applying a voltage over a range keeping the temperature constant. Both the procedures have been adopted in the present investigation on electrical conduction.

Current-voltage characteristics at different temperatures were traced by applying a voltage in the range 1.5 - 99 V. When the film equilibrated at a particular temperature, a voltage was applied. The current was found to decrease first rapidly and then slowly to reach the steady value in about 15 mins. The voltage was varied in steps of 1.5 V upto 9 V and then in steps of 9 V upto 99 V.

Current-temperature curves of various films were obtained by heating the sample at a rate of $1^{\circ}\text{C min}^{-1}$. A voltage of 9 V was applied to the film and the steady state current was secured. The currents were noted at regular intervals of

temperature.

2.10 Thermally stimulated discharge current measurement

When the film equilibrated at a desired temperature, an electric field was applied for 15 min. and was cooled with the field still applied to about 30°C in next 30 min. The thermoelectret thus formed was short circuited for 2 min. to minimise the stray surface charges. The electrets were heated at a linear heating rate to observe the thermally stimulated discharge current. Generally the heating rate was kept 0.08 Ks⁻¹. For the variation of heating rate, the electrets were also heated at 0.17 and 0.30 Ks⁻¹ rates. Thickness variation was studied by employing films of 10, 20 and 30 μm thicknesses. Films grown upon Al, Cu, Pb, Sn and Mo substrates were used to investigate the electrode effect.

2.11 Photodepolarization current measurement

Photoelectrets of pure and iodine doped PVAc films were fabricated by applying an electric field for desired time in the presence of UV illumination. The electrets so formed were preserved in dark for 1 min. to reduce stray surface charges and were depolarized by the same radiation. Photoelectrets of films grown on Al, Cu, Pb, Sn and Mo substrates were depolarized to investigate the electrode effect on photodepolarization current.

2.12 Capacitance and loss factor measurement

Dielectric properties of polymer films are investigated by measuring simultaneously the capacitance and the loss factor over a wide range of frequencies and temperatures. When the film equilibrated at a desired temperature, the capacitance and the loss factor were measured by varying the frequency in audiofrequency range. To study the effect of dopant concentration, PVAc films incorporating various concentrations of iodine were employed in the investigation.

CHAPTER III

Ram Adhar Shiv Adhar Stores

ELECTRICAL CONDUCTION

3.1 Introduction

Most of the polymers are considered to be insulators because they show low conductivity, low dielectric loss and high breakdown strength¹⁰⁷. However, recent research in the field of polymers has led to the development of special types of high molecular weight materials which exhibit a conductance high enough to class them as semiconductors (specific conductivity = 10^{-12} to $10^2 \text{ Ohm}^{-1} \text{ cm}^{-1}$) or even in some cases as conductors¹⁰⁸.

In past several years, a good amount of work has been reported on electrical conduction in polymeric materials¹⁰⁹⁻¹¹¹ and various mechanisms such as ionic conduction¹¹²⁻¹¹⁴, Schottky emission¹¹⁵⁻¹¹⁷, space charge limited conduction^{118,119} tunnelling¹²⁰, Poole-Frenkel mechanism¹²¹, charge hopping¹²² and small polaron mechanism¹²³ have been proposed to explain the experimental results.

Electric current is an ordered (i.e., having a definite direction) motion of electric charges in space. Current appears in matter under the effect of applied voltage, the charged material particles of the matter being brought into the state of ordered motion by the forces of an electric field. Thus any matter will be conductive if it contains free charge carriers. When ions move in an electric field, electrolysis takes place. Dielectrics with ionic conduction are also subjected to electrolysis but it is not so pronounced due to their high

resistivity. A large quantity of electricity can be passed through them only during a long period of time if a rather high voltage is applied. Electrolysis in dielectrics is more prominent at increased temperatures when the resistivity of matter is reduced. The molecules of most of organic polymers can not be ionized but ionic conduction still takes place due to presence of impurities. Nonohmic conduction at high fields in ionic model is explained by diffusion over field perturbed potential barriers, by internal heating and by polymer structure modification by the field. The exponential temperature dependence and disproportionality between current and voltage are usually explained on the basis of temperature and field dependence of mobility. In that case, current-voltage curves follow a hyperbolic sine-function. But it is not a definite proof of ionic conduction¹⁰⁸. In polymers with halogens in their molecular structure, electrical conductivity is qualitatively proved to be ionic¹¹³.

The fact that electronic conduction plays a role in polymers was established experimentally by Seanor¹²⁴. To discuss electronic conduction it is necessary to investigate the generation of free carriers and their transport through the material. Several books and reviews¹²⁵⁻¹²⁹ deal with the problem of carrier generation. Contact limited emission was first studied for the metal - vacuum interface. In this case three mechanisms of current flow may be distinguished. Thermionic emission¹³⁰ (Schottky emission) occurs in the low-field high-temperature

limit. Field emission^{131,132} (Fowler-Nordheim tunnelling) occurs in the high-field low-temperature limit and is the direct quantum mechanical tunnelling of electrons from allowed states below the fermi level in a metal into allowed states in vacuum. Thermal-field emission¹³³⁻¹³⁵ occurs when the dominant contribution to the observed currents arises from the tunnelling of thermally excited electrons through the narrow upper region of the image-force-lowered work-function barrier. Murphy and Good¹³⁶ showed that each of these mechanisms is a limiting approximation observed under appropriate conditions of applied field and temperature.

In polymers at or below room temperature, the density of free charge carriers is extremely low and with an electric field, non-equilibrium conditions can be achieved, which can be easily enhanced by injecting a charge through an ohmic contact. If the contact is equivalent to sufficiently large reserve of free charges, the current-voltage characteristic does not depend on the manner in which the charges are generated but is strictly connected with the charge transport mechanism. Current-voltage curve is generally nonlinear on account of two basic causes. At high fields the charges are accumulated between the electrodes¹³⁷. The presence of traps within the forbidden gap reduces the free charge density and produces a localized charge density within the polymer. The density, energy distribution and nature of the traps have a determining influence on current-voltage characteristic which also depends on the type of charges involved in the conduction

process. Space charge limited current theory of Rose¹³⁹ has been modified by Lampert¹⁴⁰.

Trapping sites exert a strong influence on the current flow i.e. the concentration of free carriers and their mobility. Mobility values in polymers are very low suggesting strong trapping. Phenyl rings and aliphatic or aromatic groups may be active traps. The trapping ability of unsaturation sites in the chains and at the chain ends of pure polymers is confirmed. Similar conclusions are obtained by Perlman and Unger¹⁴¹ in the studies of electron traps in irradiated polyethylene and teflon. Mobility values of polyethylene satisfy the relation for carrier hopping between localized sites. If the activation values of hopping are low 0.2 - 0.3 eV, hopping is connected with charge jumps brought about by motions of chain elements and the process is related to so called chain hopping mechanism while of greater values (0.5 eV) the so called trap hopping mechanism is involved. Martin and Hirsch¹⁴² proposed energy traps 0.2 - 0.75 eV for polystyrene and 0.2 - 0.3 eV for polyethylene terephthalate, showing that both mechanisms play a significant part. Life time of carriers in traps depends on the field. Thus band model with traps of various depths explains experimental results reasonably. However, the nature of charge carriers and trapping sites has not yet been settled conclusively.

In the case of polymers where H-atoms in the backbone chains are replaced by larger aromatic groups with π -electrons, the highest filled and the lowest empty molecular

orbits are formed from the substituents and the charge transfer occur within the pendent groups where charge carrier density is higher due to higher affinity to electrons or holes. The role of backbone chain is less important. Taking into consideration that the overlapping of π -systems is small, the band width must be narrow. The band width depends on the method used but does not exceed 0.1 eV. This narrow band width is responsible for the fact that the electrons are for quite a long time connected with the particular π -system which exceeds the vibrational and the high frequency dielectric relaxation time. This results in deformation of electron density in the π -system and in induced polarization of the neighbouring π -systems. The bonding energy of an electron to the potential well can be calculated. Thermal energy (Phonons) can be transferred to electrons, inducing thermally assisted hopping. This mechanism is called small polaron mechanism¹⁴³. In polymers conduction can be explained in terms of small polaron mechanism and in some cases as intrinsic phenomenon.

The trapping capability of a polymer can be greatly modified by doping it with certain impurities. Carrier mobility in polymeric materials is increased by small molecules such as iodine¹⁴⁴. Recently Srivastava and Coworkers⁷²⁻⁷⁴ doped polystyrene with several impurities and found that the conductivity of the polymer is greatly enhanced due to doping of the matrix with iodine⁷⁵. The enhanced conductivity of the polymer has been interpreted in terms of charge-transfer complexes.

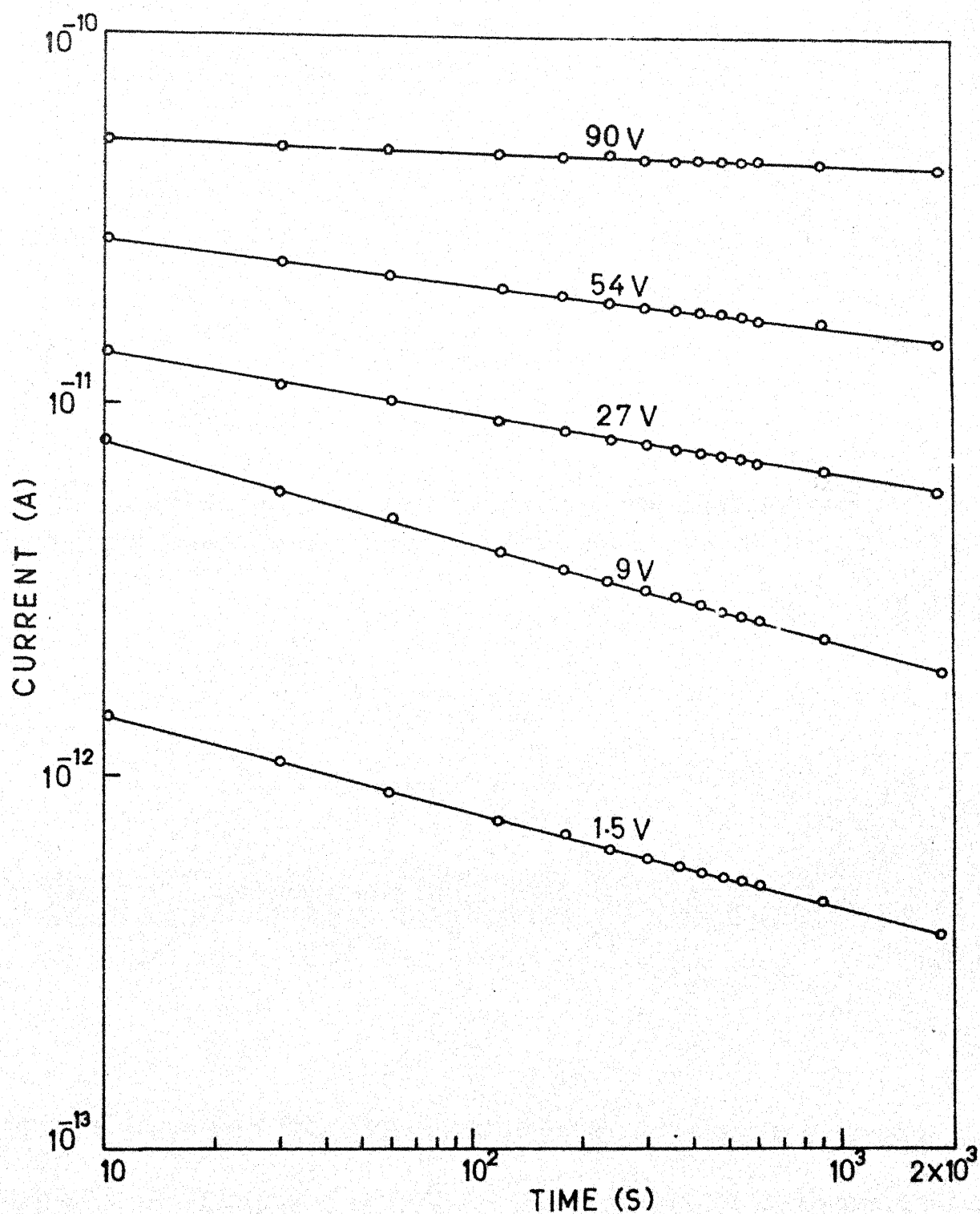


Fig.3.1—CURRENT—TIME CHARACTERISTICS OF 20 μm THICK PVAc FILMS AT 20°C FOR DIFFERENT BIAS VOLTAGES.

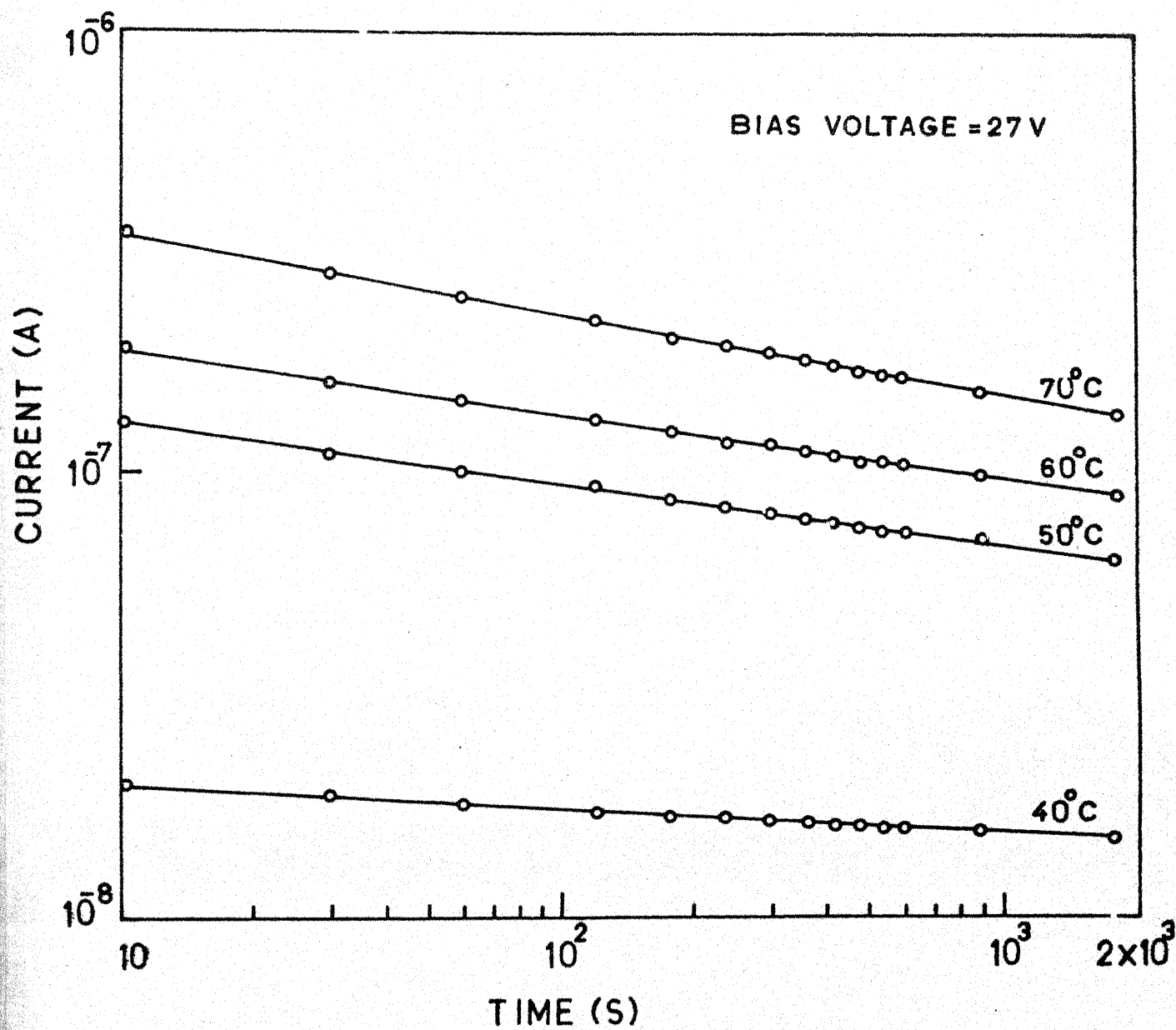


Fig.3.2—CURRENT—TIME CHARACTERISTICS OF 20 μ m THICK PVAc FILMS AT VARIOUS TEMPERATURES.

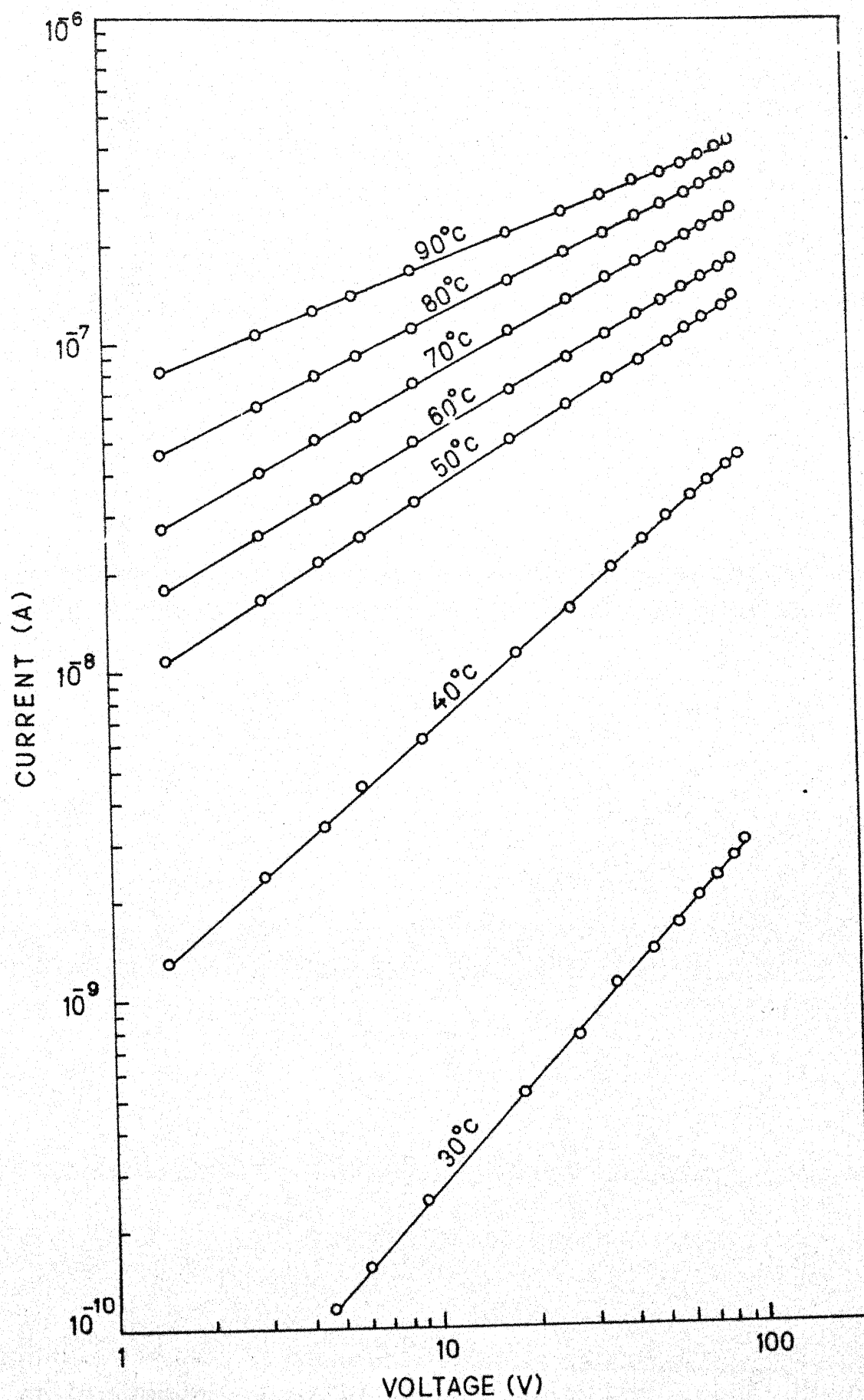


Fig.3.3 CURRENT-VOLTAGE CHARACTERISTICS OF 20 μ m THICK PVAc FILMS.

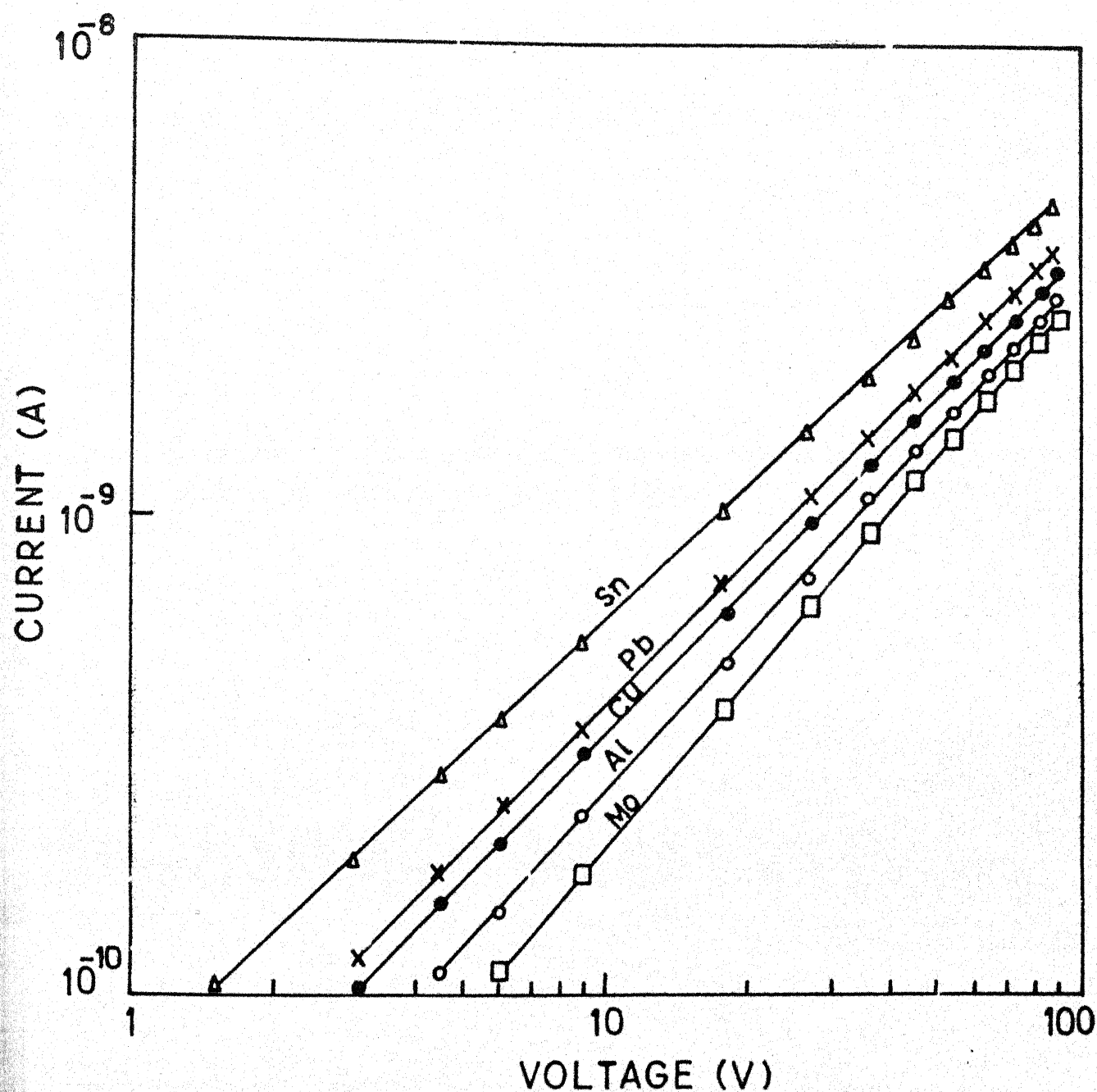


Fig.3.4—CURRENT—VOLTAGE CHARACTERISTICS OF 20 μm THICK PVAc FILMS AT 30°C IN CONTACT WITH DIFFERENT METALS

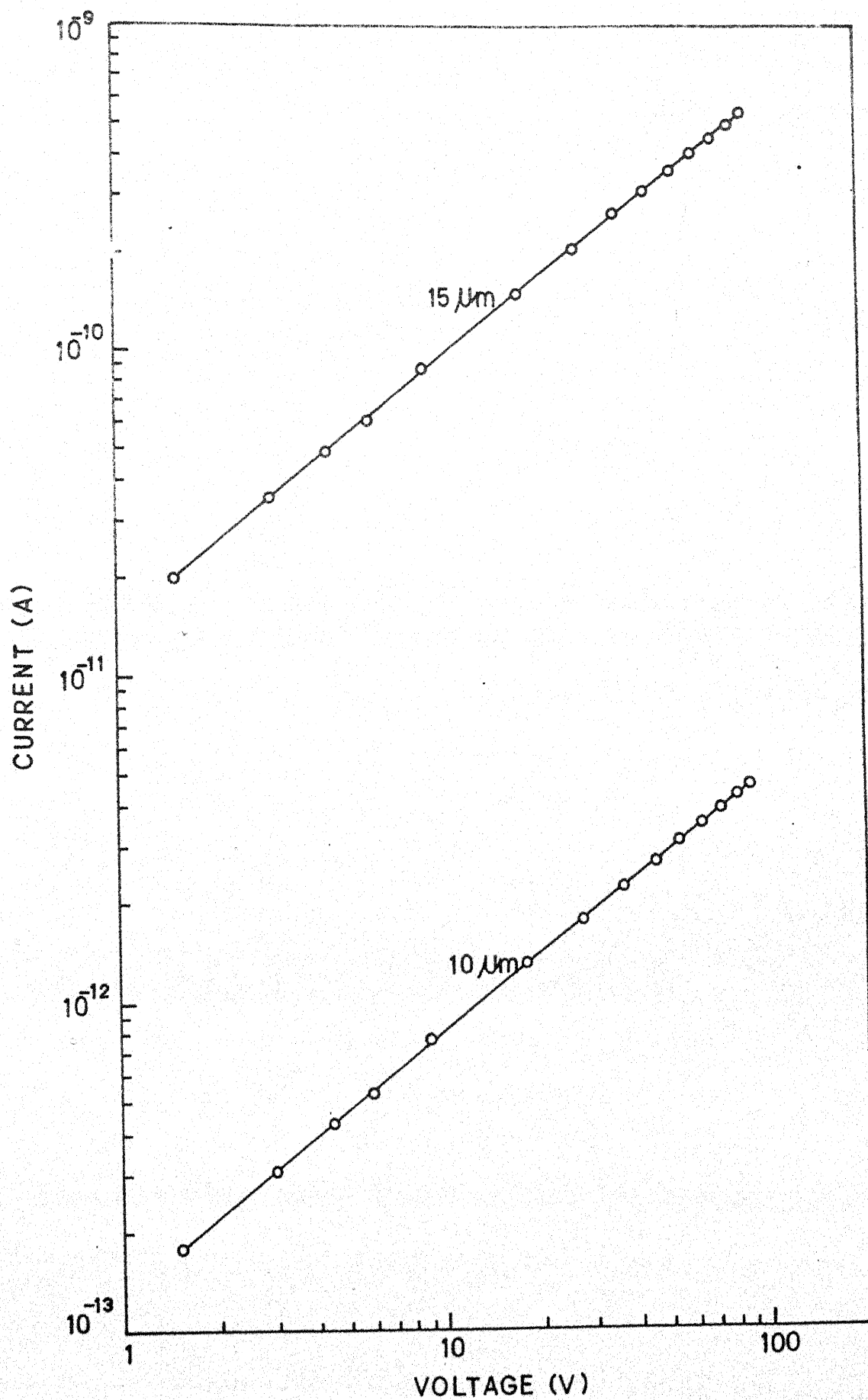


Fig. 3.5—CURRENT-VOLTAGE CHARACTERISTICS OF 10 AND 15 μm THICK PVAc FILMS AT 40°C.

This chapter describes transient behaviour of current, current-voltage characteristics and temperature dependence of current in pure and iodine doped PVAc films.

3.2 Results

Application of a voltage to PVAc film at a particular temperature gave a current which was found to decrease with time. The influence of voltage and temperature on transient current was investigated. The substrate was biased positively and the upper electrode was connected to the electrometer. The current versus time on a double log scale yielded a straight line. These lines at 20°C for voltages 1.5, 9, 27, 54 and 90 V are shown in fig 3.1. The slope of the straight line decreases with the increase in voltage applied. Fig 3.2 exhibits current as a function of time at a voltage of 27 V for 40, 50, 60 and 70°C temperatures. The slope of the line increases as the temperature is increased.

Current-voltage characteristics of 20 μm thick PVAc films at 30, 40, 50, 60, 70, 80 and 90°C are shown in fig 3.3. The voltage was varied in the range 1.5 - 99 V. The curves are seen to be straight lines. The slope of the line decreases with the increase in temperature. Electrode effect on current-voltage characteristics of PVAc was investigated at 30°C by employing Al, Pb, Cu, Sn and Mo substrates which were biased positively. Fig 3.4 illustrates the effect of electrode material on current versus voltage curve. Fig 3.5 contains current-voltage characte-

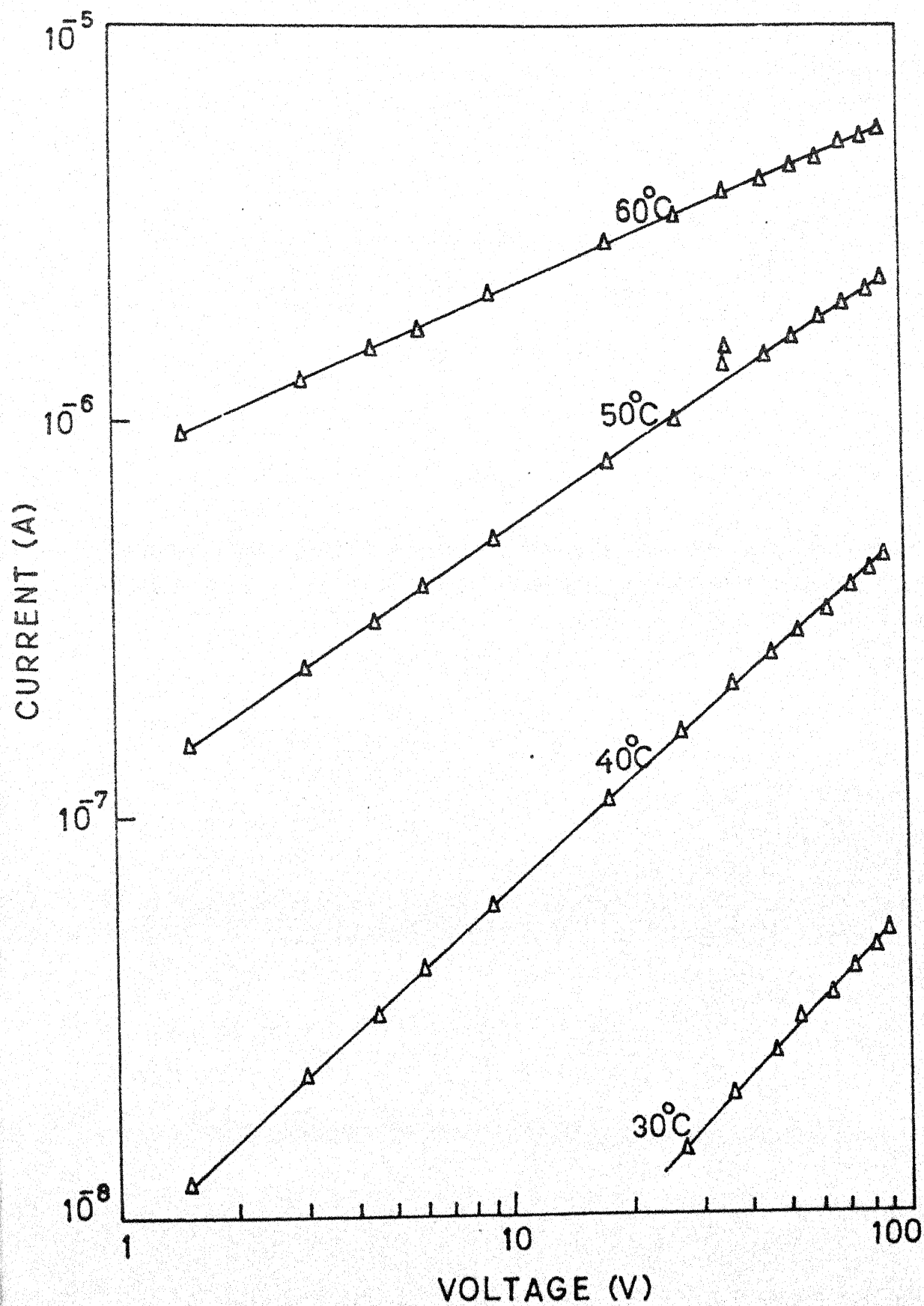


Fig.3.6—CURRENT—VOLTAGE CHARACTERISTICS OF 20 μm THICK 10 g l^{-1} IODINE DOPED PVAc FILMS.

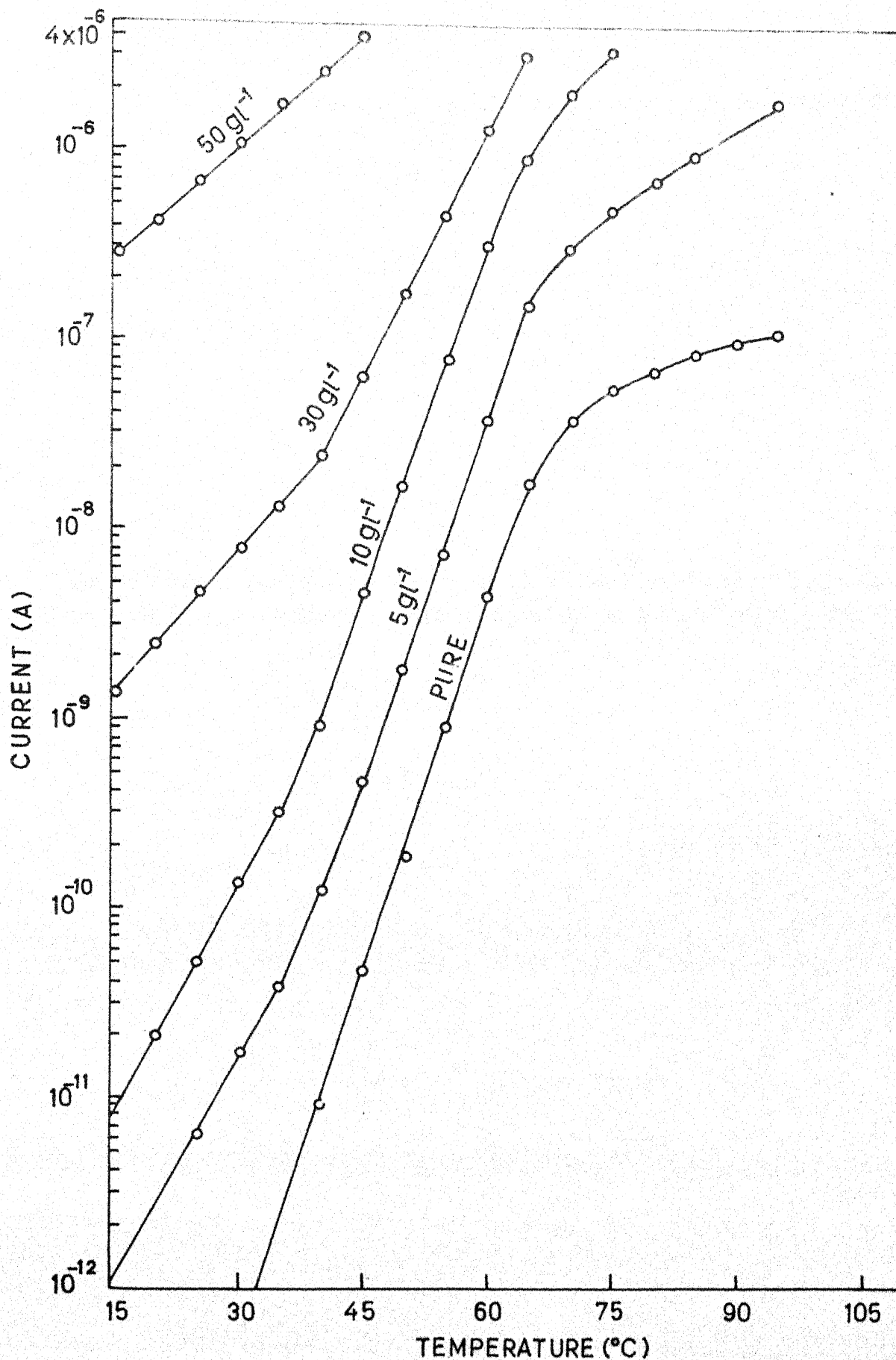


Fig.3.7—CURRENT vs. TEMPERATURE FOR PURE AND IODINE DOPED PVAc FILMS.

ristics of 10 and 15 μm thick PVAc films at 40°C while that of 20 μm thick film has been described in fig 3.3. Current versus voltage curves of films of various thicknesses are seen to be parallel. At a particular voltage the current is decreased with the decrease in film thickness. Current-voltage characteristics of 10 gl^{-1} iodine doped PVAc films at 30, 40, 50 and 60°C are depicted in fig 3.6. The curves are seen to be straight line plots. The slope of current-voltage plot diminishes with the rise in temperature.

The effect of iodine concentration on electrical conductivity of PVAc was investigated by heating the sample at a uniform rate of 1°C min^{-1} . A potential of 9 V was applied to the film and when the current assumed the steady value, the sample was heated. Current versus temperature curves for pure and 5, 10, 30, 50 gl^{-1} iodine doped PVAc films are shown in fig 3.7. At a particular temperature the current is enhanced due to increase in concentration of iodine incorporation in the polymer. The current-temperature curve of PVAc film is linear upto about 65°C beyond which it bends heavily. Incorporation of iodine in 5 gl^{-1} creates a kink round 35°C in current-temperature curve of PVAc. As the dopant concentration is increased, the kink is shifted slightly to a higher temperature. This kink appears at about 40 and 45°C respectively for 10 and 30 gl^{-1} concentration of iodine. At 50 gl^{-1} concentration of iodine the kink disappears and the current increases linearly with temperature.

3.3 Discussion

Electronic conduction may be due to the motion of free carriers, electrons in the conduction band and holes in the valence band or alternatively to the motion of quasi-localized carriers which is otherwise described as hopping of bound carriers between localized sites¹⁴⁵ in the dielectric. The former process requires an activation energy in order to excite a carrier into the relevant band and this energy can normally be supplied thermally or by other free carriers which have acquired a high energy in an electric field, leading to an avalanche process. The activation energy may be affected by electric field as in the case of Poole-Frenkel effect¹⁴⁶.

The hopping process requires less energy than the activation into the free band and this energy may, in the limit of very high density of localized centres, tend to zero as in the case of impurity band conduction in semi-conductors¹⁴⁷. This process is favoured in the case of heavily disordered solids, such as amorphous and glassy dielectric films¹⁴⁸.

Some dielectrics show a region of linear current-voltage characteristics i.e. ohmic conduction at low fields¹⁴⁹, specially at elevated temperatures although more often this region can not be seen at the limit of detection. It is difficult to establish conclusively whether ohmic conduction is due to ionic or electronic processes but ionic conduction would appear more likely.

In interpreting the properties of dielectric films,

one frequently employs concepts taken over from the physics of crystalline media. In this way one refers to trapping levels and donor and acceptor levels at discrete energy values. One speaks of energy barriers due to ionized impurities and, in the case of Poole-Frenkel effect one employs the model of hydrogenic impurities in which the bound electron is characterised by a definite effective mass and a ground state orbit of a diameter corresponding to several interatomic spacings. These concepts may be valid to a greater or lesser extent in the case of poly crystalline and micro crystalline films, although allowance may have to be made for the presence of interfacial barriers. It would be very difficult to justify their use in application to amorphous and glassy films. It is appropriate to recall here the salient features of the theory of amorphous conductors as it applies to dielectric films. The general consensus of opinion is that the basic features of the band structure, such as the width of the forbidden gap, are determined primarily by the short-range order i.e. by the relative disposition of the nearest neighbours in the solid. Since these dispositions are similar in amorphous and crystalline solids, the broad features are preserved on transition from crystalline to amorphous structure. The disappearance of medium and long range order does influence the detailed shape of the band structure; however, in that case it causes a considerable blurring of the edges of the conduction and valence bands, and gives rise to a distribution of deep localized levels in the forbidden gap.

In a crystalline solid, there exists a clear distinction between the propagating bands—conduction, valence and forbidden. In the former the carriers propagate freely except for collisions on thermal vibrations and other lattice imperfections which determine a mean free path which is greater, usually considerably greater than the lattice spacing. In the forbidden gap, the energy levels that may exist due to imperfections are strictly localized and an electron has to be excited from one of these levels to the conduction band before being able to move on. Special cases arise when the localized levels are spaced so closely that their wave functions overlap and give rise to the formation of the so called impurity band, leading to metallic properties with zero activation energy. Alternatively, the spacing may not be as close as is necessary for the formation of an impurity band, but sufficient for phonon-assisted tunnelling between neighbouring centres, the so called hopping conduction. Hopping is characterised by an activation energy which is only a fraction of the normal ionization energy of the carrier from the centre into the band and is often accompanied by a rather complicated frequency dependence.

The significance of the blurred band edges is that there is no sharp distinction between the propagating and forbidden gap but instead partly localized levels are formed leading to a conduction by a process intermediate between impurity band and hopping conduction in which the propagation of carriers is characterized by a small mobility. The deeper

the levels, the more localized their character, until the deep tail states may be considered as proper trapping sites, unlike traps in crystalline materials; however, these deep states would not possess any clearly defined activation energy.

Poole-Frenkel mechanism is frequently invoked in the interpretation of electric current in dielectric films at reasonably high electric fields. The physical basis of Poole-Frenkel mechanism is analogous to the Schottky emission.

O'Dwyer¹⁵⁰ in a theoretical paper considers a detailed electronic model of a dielectric with traps with Schottky emission from an injecting electrode and with Fowler-Nordheim correction for tunnelling through the top of the barrier at high fields. In a recent review of Poole-Frenkel mechanism Simmons¹⁵¹ points out that experimental data apparently favouring the Schottky mechanism can be made more compatible with Poole-Frenkel mechanism if it is postulated that shallow neutral traps are present in the dielectric together with deep lying donors. Franks and Simmons¹⁵² consider further the effect of space charge on Poole-Frenkel process.

A consequence of the phenomenon of carrier injection is the formation of a space charge cloud¹⁵³ of carriers in the vicinity of contacts. Mutual repulsion between the individual carriers limits the total injected charge in the film and the resulting current is said to be space charge limited. Trapping sites reduce the magnitude of current. The mobile charge carriers are continually interacting with the lattice. A thermodynamical

equilibrium is maintained between the space charge and lattice so that there is a special relationship between the electric field and the drift velocity of the carriers. The trapping sites accentuate this difference even further. Holes or electrons can be injected according to the choice of electrode material¹⁵⁴. This then brings in the added complication of recombination.

3.3 (a) Transient Current

When a d.c. field is applied to a finite thickness of a dielectric sandwiched between two parallel electrodes, there is, besides the rapidly charging current and steady state conduction current, a long term slowly decaying current. Similarly on removal of the voltage and the electrodes short-circuited, the fast component of the current is followed by a long term slowly decaying current. This long term current is known as the anomalous current or absorption current¹⁵⁵. Provided that the principle of superposition holds, the behaviour of change in current with time for the charging and discharging events are equivalent and their numerical analysis are identical. The discharge current manifests itself in the familiar absorption of the charging experiment. Dielectric relaxations which occur in the frequency range 0.1 Hz are normally studied by their contributions to the current decay of a charged dielectric on discharge¹⁵⁶.

Das Gupta and Joyner¹⁵⁵ reported absorption current in polyethylene terephthalate and polypropylene by varying field,

temperature, time, electrode material and thickness and identified the mechanism from the possibilities—electrode polarization, dipole orientation, charge storage leading to trapped space charge effect, tunnelling of charge carriers from the electrodes and hopping of charge carriers through localized states. The behaviour of absorption current in PVAc is observed to be similar to that of polypropylene. A sudden increase in voltage causes the current to transiently increase to high values. In a matter of minutes, the current subsides to a much smaller stationary value. The interpretation is that the sudden increase in voltage forced a corresponding increase of charge in the conduction band. In the course of minutes, most of this free charge settles into traps and one observes the rapid decay of current. The time required for the transient current to subside is a direct measure of the capture cross-section of traps for free carriers.

The transient current J versus time t on a double log scale yields a straight line (figs 3.1 and 3.2) showing that the decaying current obeys the usual t^{-n} law (n : an exponent; $0 < n < 1$) before reaching a steady state. The field dependence of the current (fig 3.1) may be expressed by the relation :

$$J(t) = K(t) E^p \quad \dots (3.1)$$

where K is a decay factor independent of the field E and p is found to be 0.9 at low applied fields. The value of p decreases with the increase in voltage. The temperature dependence of current (fig 3.2) may be described by

$$J(t) = A(T) t^{-n} \quad \dots (3.2)$$

where A is a temperature dependant term. The absorption current shows a marked increase with temperature. The observed magnitude of n in the temperature range and the absence of any thickness dependence and any significant electrode material effect rule out tunnelling, electrode polarization and charge injection forming trapped space charge as possible mechanisms for absorption currents. The observed behaviour of absorption current in the temperature range may be explained either by the mechanism of dipolar relaxation in the bulk with a wide distribution of relaxation times or by a charge carrier hopping process through localized states. A relaxation of dipoles may also be ruled out as a relevant mechanism because the absorption current was not found to be inversely proportional to the sample thickness¹⁵⁷.

3.3 (b) Electrode Material Effect

Charge transfer from metal depends on electron levels in which the carriers shift freely under the influence of field. The energy on this level¹⁵⁸ may be given by :

$$E_b = E_g = (I_g - p^+) - (A_c + p^-) = I_c - A_c \quad \dots (3.3)$$

where I_g is ionization energy, A_c electron affinity, p^+ and p^- polarization energies and I_c ionization energy of a molecule of the material, E_b corresponds to energy gap E_g . In case of

polystyrene $E_b = E_g = 4-5$ eV while for polyethylene $E_g \approx 8$ eV ($p^+ = p^- \approx 1.5$ eV).

From these data intrinsic generation of free carriers resulting from Boltzmann's factor $\exp(-E_g/kT)$ is negligible at temperatures below polymer decomposition. It gives more emphasis to the importance of metal-electrode contact which is the origin of carriers responsible for conduction.

The contact is said to be ideal if the distance between metal and dielectric is 10 \AA . If no excess ions or other energy states appear in the dielectric, the fermilevel is midway between conduction and valence bands. The fermilevel is away from the vacuum level by ϕ (ϕ corresponds to work function of electron detached from the metal). When the metal comes into contact with the dielectric, there is a tendency towards equalization of levels at the point of contact. If the fermi level is higher in the dielectric than in the metal, then electrons are transferred to the metal and in this way a levelling of potentials takes place. In the case of organic compounds, there are no excess charges even if there are defects; they are deep and therefore can not go ionization under the influence of thermal energy, the same applies to impurities from other organic molecules. Electrostatic equilibrium is established only due to transfer of carriers from metal. Electron overcomes the potential barrier

$$\chi^- = \phi - A_c \quad \dots (3.4)$$

while holes

$$X^+ = I_c - \phi \quad \dots (3.5)$$

In this way emission current arises as described by Richardson's equation :

$$J = A T^2 \exp \left(- \frac{X}{kT} \right) \quad \dots (3.6)$$

A similar equation holds for holes. Such an injected charge is captured in neutral traps which are always present. Fig 3.4 exhibits the lack of significant electrode effect on current-voltage characteristics of PVAc films.

3.3 (c) Thickness Dependence

It is of importance to be able to distinguish between non-ohmic behaviour due to space charge and that arising from other physical process. The obvious method is to investigate the dependence on thickness of a set of current-voltage curves. Current-voltage characteristics of 10 and 15 μm thick films at 40°C are shown in fig 3.5 while that of 20 μm thick film is shown in fig 3.3. Thick film gives more current. It is the evidence of space charge accumulation. Pulfrey et al¹⁵⁹ consider electronic conduction and space charge in amorphous insulating films and conclude that at small thicknesses Schottky law is more probable while at large thickness the Poole-Frenkel law is expected. Thus, if one makes films of various thicknesses, one would expect Schottky mechanism for thinner samples and Poole-Frenkel for thicker specimens, i.e. the typical transition

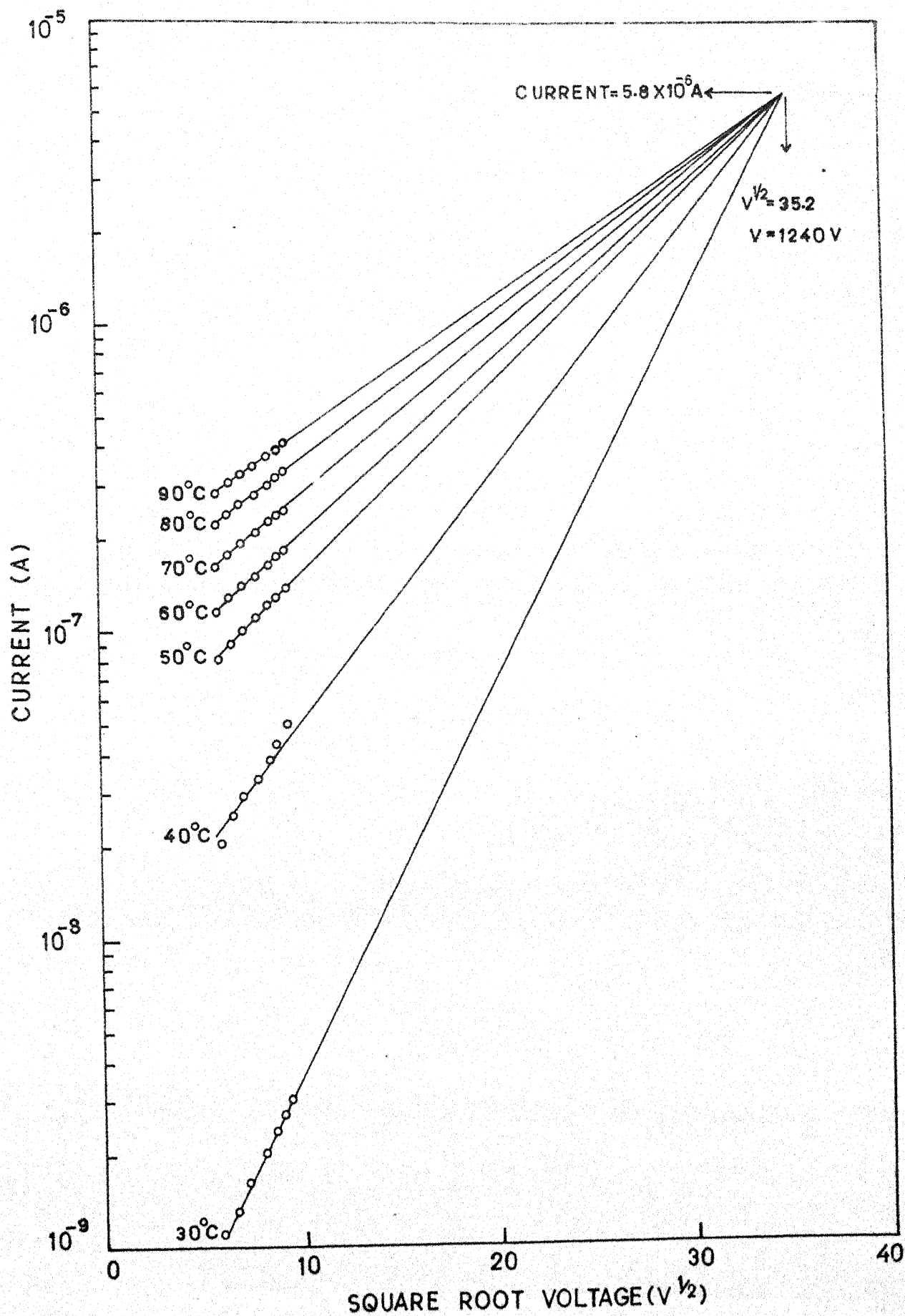


Fig. 3.8—CURRENT Vs. SQUARE ROOT VOLTAGE OF 20 μm THICK PVAC FILMS AT VARIOUS TEMPERATURES.

between interface control with thin films and typical macroscopic conduction in electrically neutral material, changing at higher currents, to space-charge limited current with the free carriers providing the space-charge.

3.3 (d) Current-voltage Characteristics

Current-voltage (J-V) characteristics of 20 μm thick PVAc films in the temperature range 30-90°C have been plotted in fig 3.3. They are all linear. When the charge carriers are supplied from the electrode and all of them are transported Ohm's law holds and the current is proportional to the voltage. The current in the case is limited by the electrode. When the electric field is low, the mobility of the carriers or the presence of traps can limit the current observed in the system. In the absence of traps only mobility limits the current and one has a super linear J-V curve¹⁶⁰⁻¹⁶².

The plots of fig 3.3 have been replotted in $J-V^{1/2}$ form in fig 3.8 for applied voltage in between 36-99 V. The plots are seen to be linear. It is a well established experimental fact that for fields in excess of some 10 kV cm^{-1} many dielectric films exhibit current-voltage characteristics of the form :

$$J \propto \exp \left(\frac{e \beta E^{1/2}}{kT} \right) \quad \dots (3.7)$$

where e is electronic charge, E the field, k Boltzmann's constant and β a coefficient. This is naturally taken as

evidence of either Schottky or Poole-Frenkel mechanism and since the coefficient β for either of these is given by essentially fundamental constants, it is claimed that it should be possible to decide between the two mechanisms from the numerical value of the coefficients. The expression for Schottky emission is

$$J = J_0 \exp \left[\frac{e (\beta_S E^{1/2} - V_g)}{kT} \right] \dots (3.8)$$

where J_0 is pre-exponential factor, V_g the potential barrier and β_S Schottky field lowering coefficient which is given by

$$\beta_S = \left(\frac{e}{4\pi \epsilon_0 \epsilon} \right)^{1/2} \dots (3.9)$$

where ϵ_0 is the dielectric constant of free space and ϵ that of the material. The field lowering of the barrier height for Poole-Frenkel effect is given by $\beta_{PF} E^{1/2}$ where $\beta_{PF} = 2 \beta_S$. The theoretical and experimental values of β show marked departures. This complicates the interpretation in terms of either of the simple models because a temperature dependence is not provided in both the Schottky and Poole-Frenkel mechanisms.

Scher and Montroll¹⁴⁵ recently advanced the phenomenological relationship for hopping conduction in which the field and temperature dependence of the mobility μ is described by the following equation :

$$\mu = \mu_0 \exp \left[\left(-\frac{a}{k} \right) (E^n - E_0^n) \left(-\frac{1}{T} - \frac{1}{T_0} \right) \right] \dots (3.10)$$

where μ_0 is pre-exponential factor, a , E_0 and T_0 are parameters

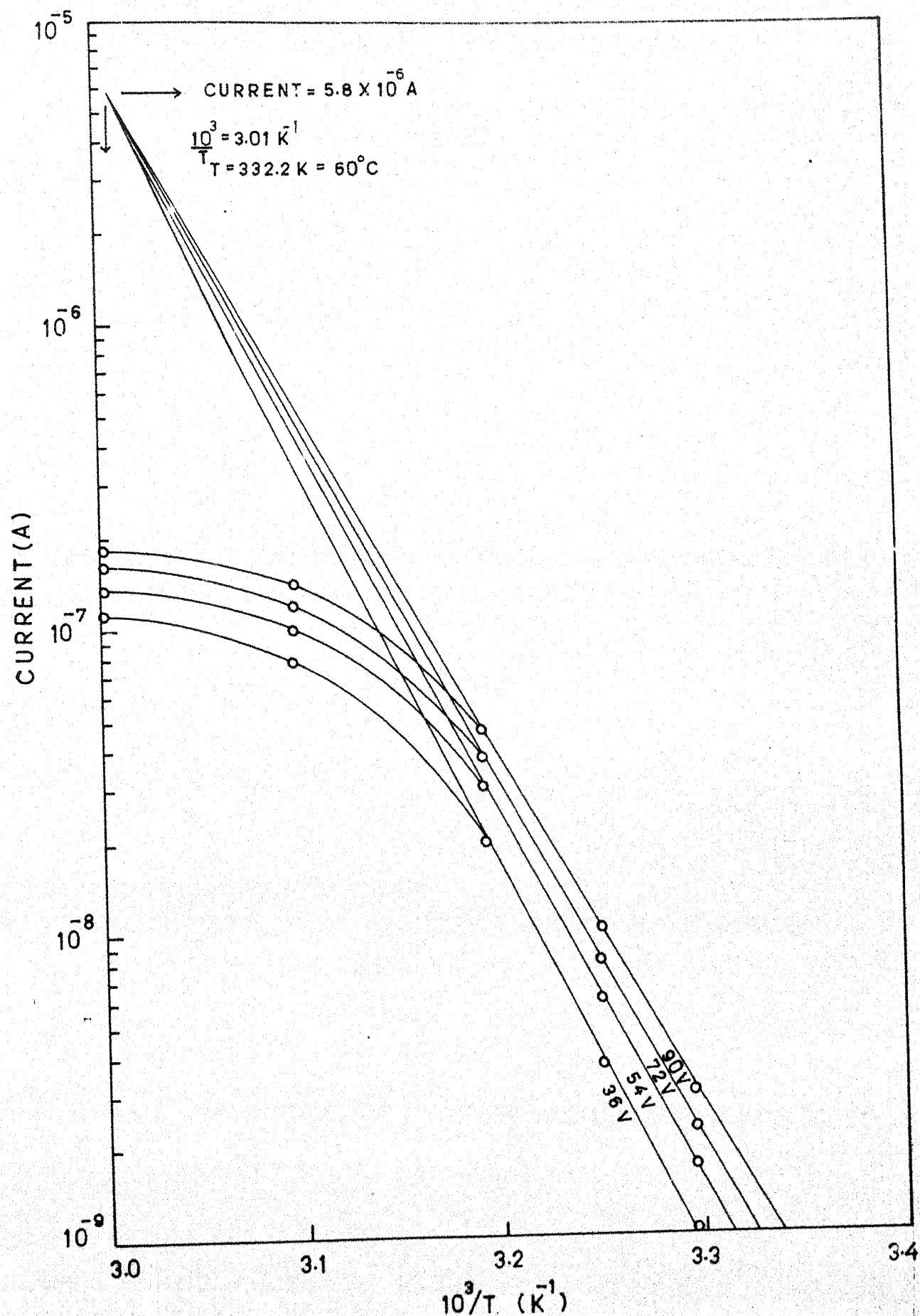


Fig. 3.9—CURRENT Vs. $10^3/T$ OF $20 \mu\text{m}$ THICK PVAc FILMS AT VARIOUS VOLTAGE.

and $n \sim \frac{1}{2}$. In fig 3.8 the square root voltage dependence of current is shown for various temperatures. The straight lines when extended have a common intercept. The values of current and voltage at the intercept are found to be 5.8×10^{-6} A and 1240 V respectively. The same results are replotted in fig 3.9 as a function of $10^3/T$ in between 30–60°C at 36, 54, 72 and 90 V. The curves bend heavily beyond 40°C. This behaviour is believed to be associated with the glass transition temperature of the polymer. The plots before 40°C are extended to have the common intercept. The values of current and temperature at the intercept are found to be 5.8×10^{-6} A and 60°C respectively. The values for current obtained from the two intercepts are in very good agreement. Therefore the current and hence, the mobility is described by equation (3.10).

3.3 (e) Effect of Doping on Current-Voltage Characteristics

Current-voltage characteristics of 10 gl^{-1} iodine doped PVAc films at 30, 40, 50 and 60°C are shown in fig 3.6. In fig 3.10 the square root voltage dependence of current is shown for various temperatures. The straight lines are extended to join at the common intercept. The values of current and voltage at the intercept are found to be 8.4×10^{-5} A and 1183 V respectively. The same results are replotted in fig 3.11 as a function of $10^3/T$ in between 30–60°C at 36, 54, 72 and 90 V. The curves bend heavily above 50°C. The straight lines meet at the common intercept. The values of current and temperature

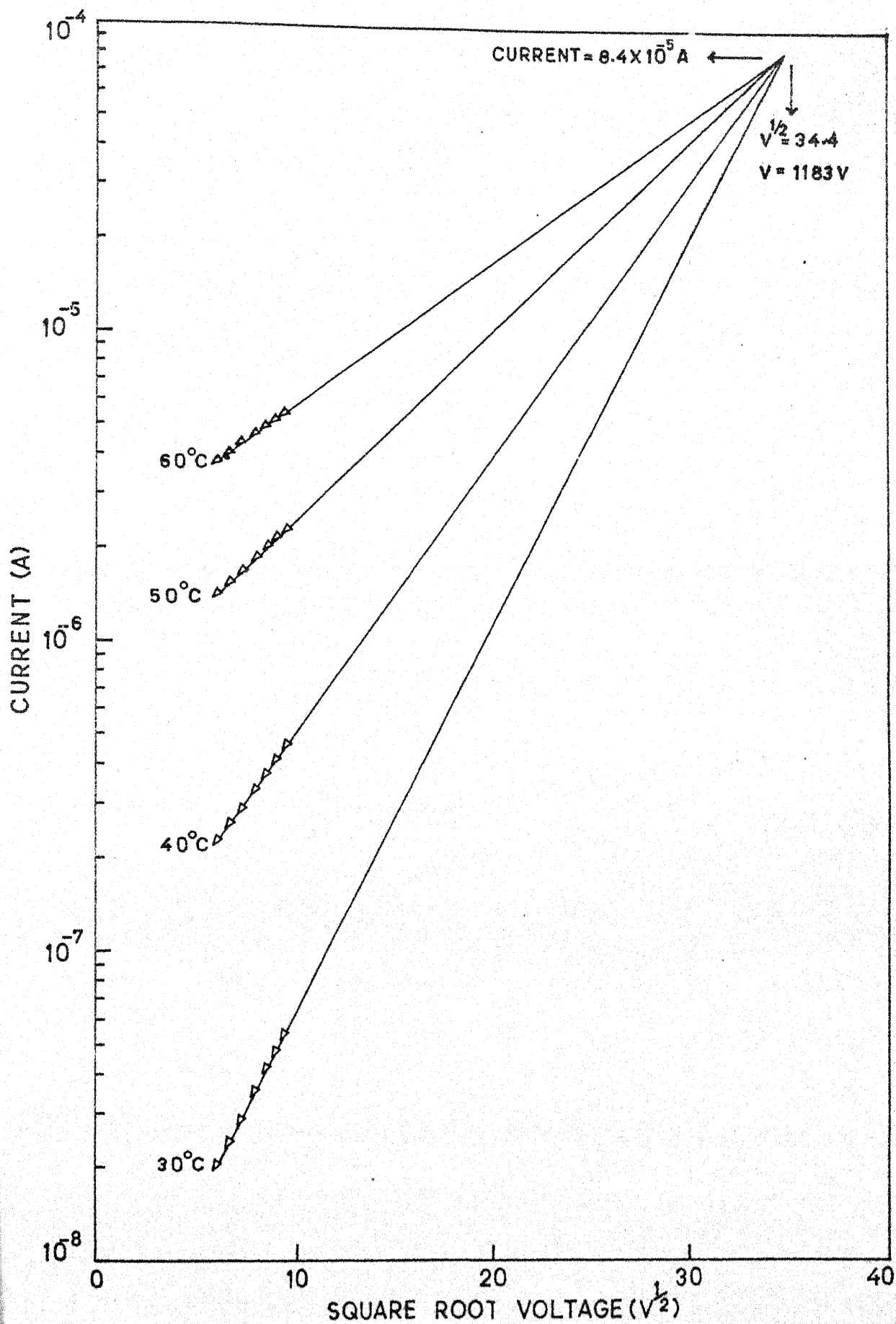


Fig.3.10-CURRENT Vs. SQUARE ROOT VOLTAGE OF 20 μm THICK
10 g/l¹ IODINE DOPED PVAc FILMS AT VARIOUS TEMPERATURE.

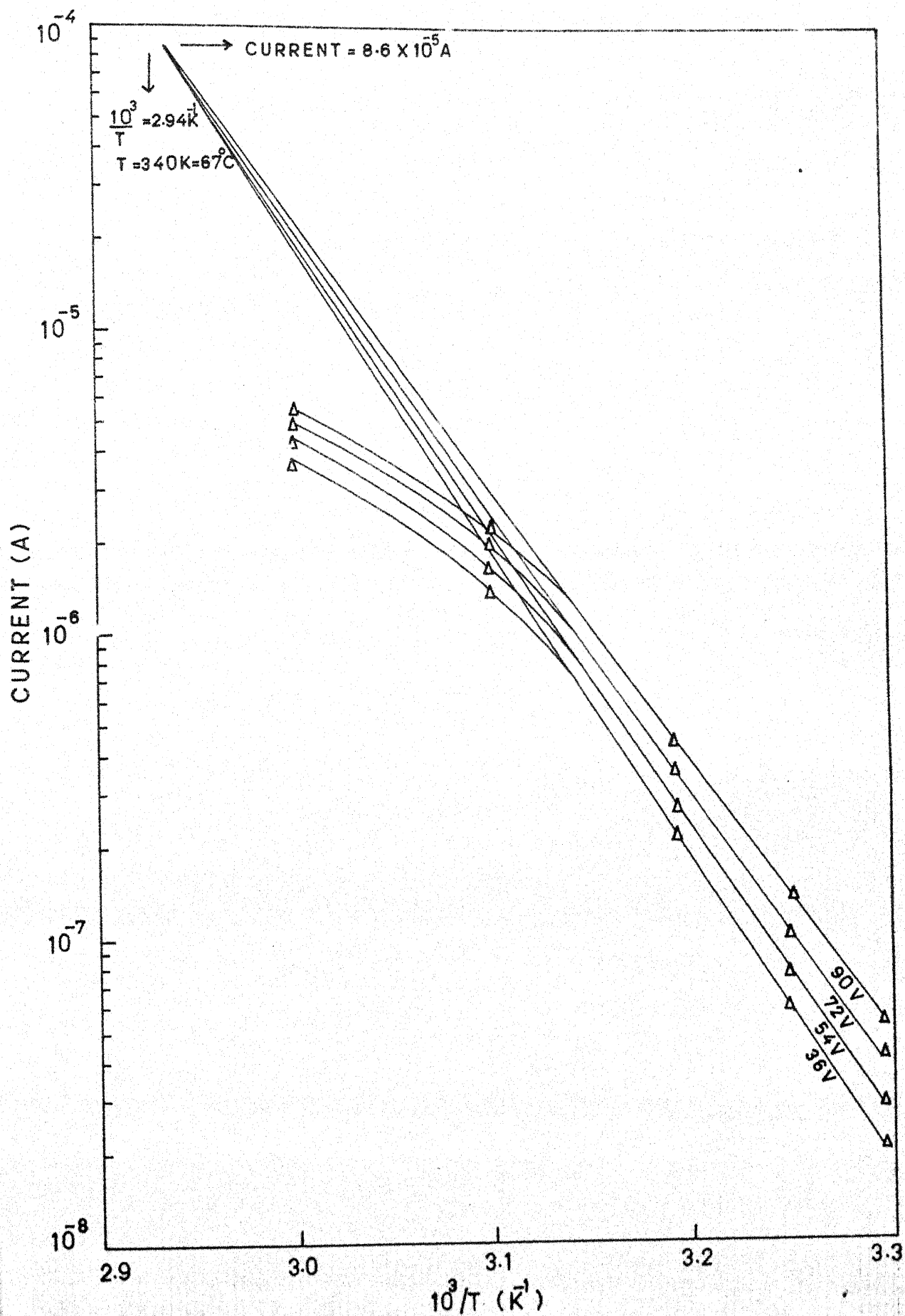


Fig. 3. 11—CURRENT Vs. $10^3/T$ OF $20 \mu\text{m}$ THICK 10 g/l IODINE DOPED PVAc FILM AT VARIOUS VOLTAGES.

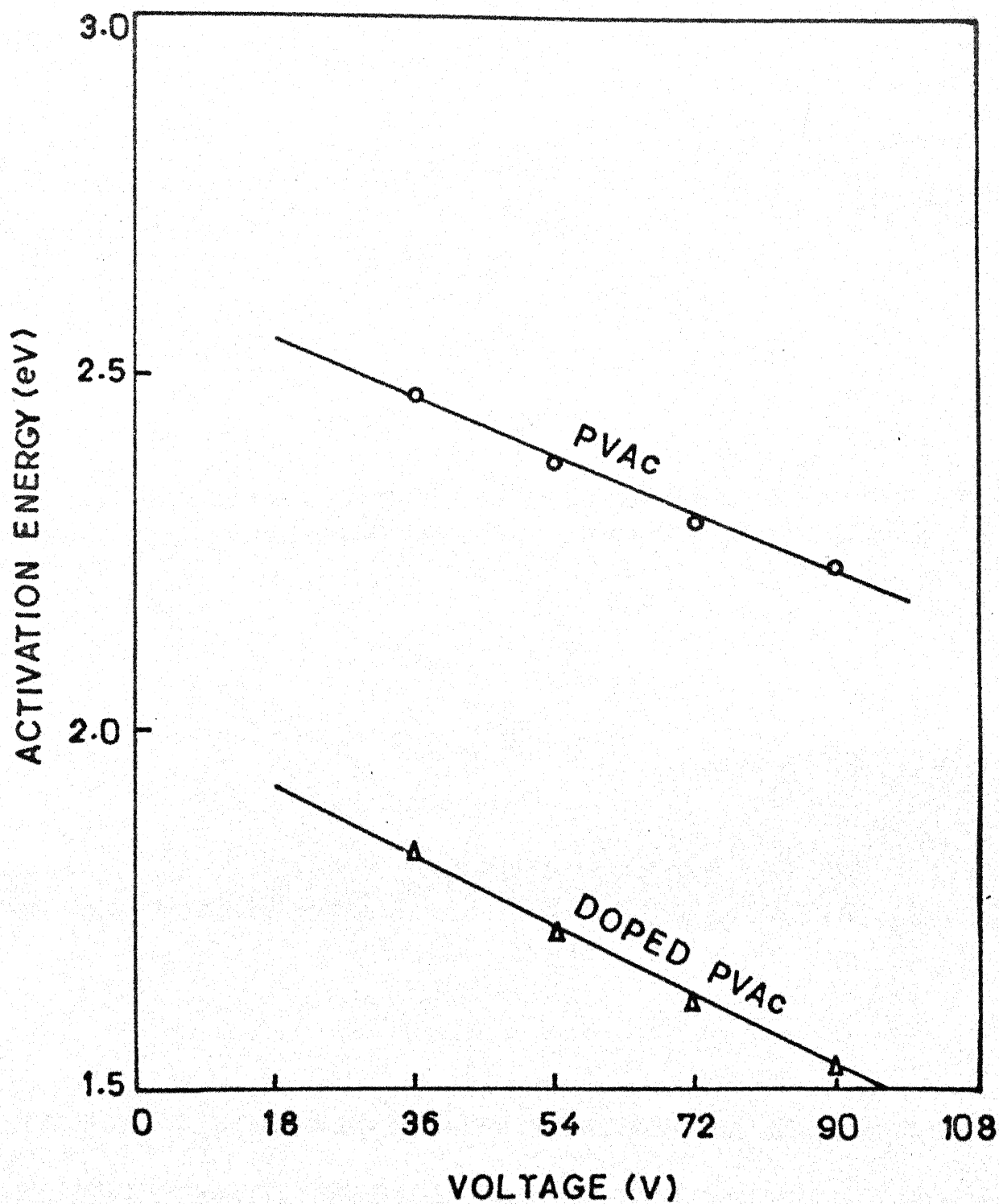


Fig. 3.12—ACTIVATION ENERGY VS. VOLTAGE FOR PURE AND 10 gI⁻¹ IODINE DOPED PVAc FILMS.

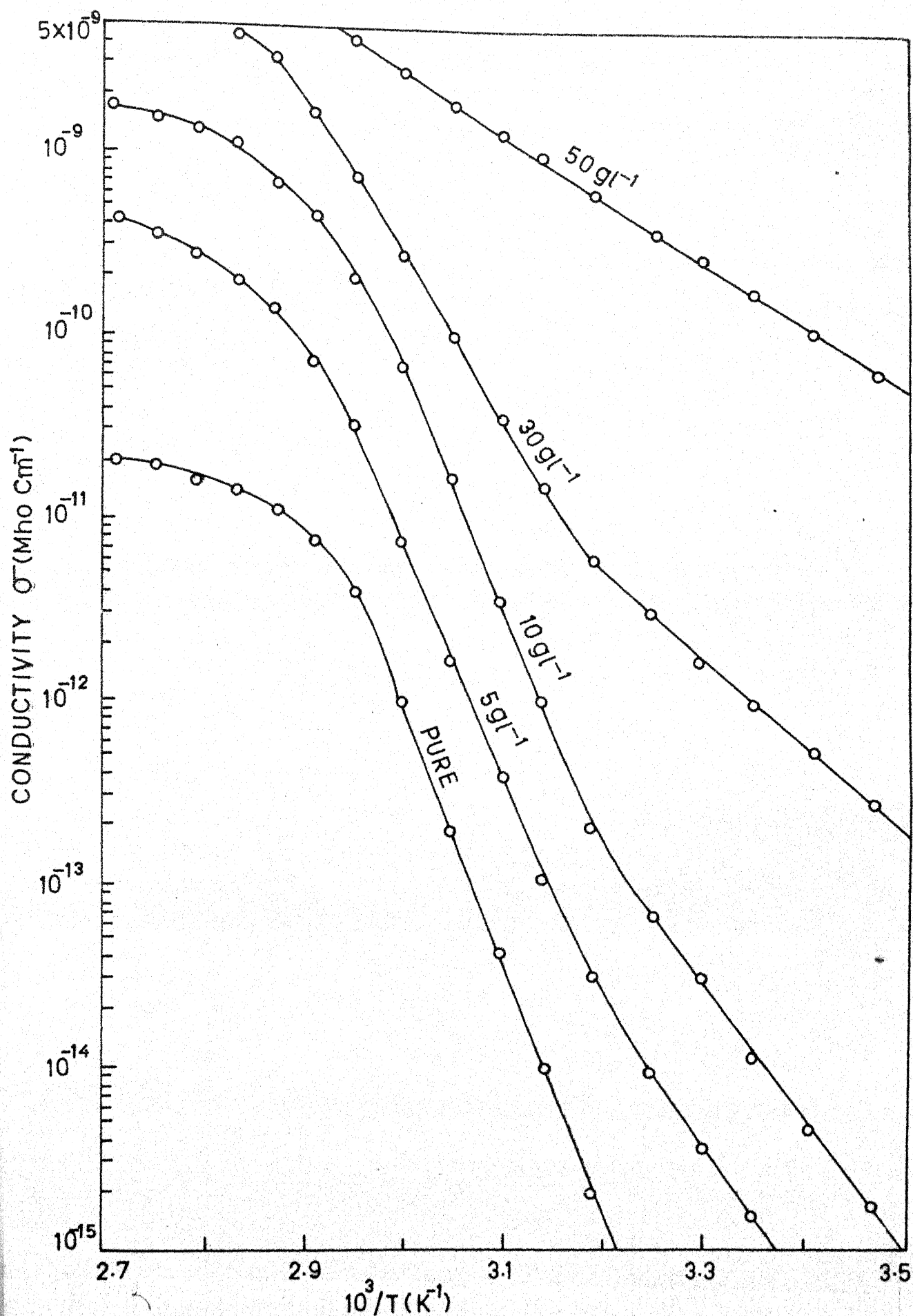


Fig. 3-13 — CONDUCTIVITY (σ) Vs. $10^3/T$ FOR PURE AND IODINEDOPED PVAc FILMS.

at the intercept are found to be $8.6 \times 10^{-5} \text{ A}$ and 67°C respectively. The values for current obtained from the two intercepts are in good agreement. So the current and hence the mobility in iodine doped PVAc film is also described adequately by equation (3.10). The value of current at the intercept for PVAc film is obtained to be $5.8 \times 10^{-6} \text{ A}$ while that for iodine doped PVAc film is determined to be $8.6 \times 10^{-5} \text{ A}$. Hence, the carrier mobility is enhanced due to doping of the polymer matrix with iodine. The values of activation energy at different voltages were calculated from figs 3.9 and 3.11 for pure and doped PVAc films respectively. The activation energy as a function of voltage for two types of samples is shown in fig 3.12. A linear voltage dependence of the activation energy is exhibited by pure and doped PVAc but the slope of the plot for doped film is greater than that for the pure one. This indicates that due to doping the activation energy becomes more voltage dependent.

3.3 (f) Effect of Dopant Concentration on Temperature Dependence of Conductivity.

The conductivity (σ) was evaluated from the measured value of current (fig 3.7). The conductivity curves (σ versus $10^3/T$) of pure and iodine doped PVAc films are shown in fig 3.13. The conductivity of PVAc increases linearly upto about 65°C . Beyond 65°C the conductivity curve bends and shows an inflection. The interpretation of the temperature dependence of conductivity in polymers is far from consistent.

Some hypotheses have postulated that conductivity above and below the inflection is ionic and electronic in nature respectively and yet others are based on the analogy with some other materials, according to which intrinsic conduction exists above inflection and impurity conductivity below inflection. Shishkin and Vershinina¹⁶³ and Warfield and Petree¹⁶⁴ connect the inflection with glass transition of the polymer. They explain the inflection at glass transition by change in environmental conditions for ion mobility at the transition from the glassy state into a highly elastic one. Herwig and Jenckel¹⁶⁵ and Reddish¹⁶⁶ suppose that the inflection appears as a result of the superposition of polarization effects on the conductivity process at temperatures below the glass transition temperature, at which the relaxation times become long. Adamec and Mateova¹⁶⁷ conclude that the inflection on $\sigma(T)$ curve does not necessarily correspond to the glass transition temperature of the polymer, even though the inherent conductivity becomes a predominating component in the vicinity of glass transition.

Incorporation of iodine in 5 gl^{-1} exhibits two regions in temperature dependence of conductivity of the polymer, one below and the other above 45°C . With the increase in dopant concentration the two regions become more prominent and at a concentration of 50 gl^{-1} the two regions terminate into one. The value of activation energy for different regions was calculated from Arrhenius relation :

$$\sigma = \sigma_0 \exp \left(-\frac{H}{RT} \right) \quad \dots (3.11)$$

where σ_0 is pre-exponential factor and H the activation energy. The low temperature tail below 45°C in conductivity curves of the doped films may be attributed to impurity conduction. The activation energy 2.63 eV of pure PVAc is decreased due to doping of the polymer. The activation energies of 5, 10, 30 and 50 gl^{-1} iodine doped films come out to be 1.67, 1.54, 0.89 and 0.66 eV respectively. The values of activation energies above 45°C are calculated to be 2.58, 2.60 and 1.74 eV respectively for 5, 10 and 30 gl^{-1} iodine doped films. High activation arises from intrinsic conduction. The difference in activation energies is due to higher dissociation energy to form the carriers for intrinsic conduction. Similar types of results have been reported due to doping of poly vinyl fluoride¹⁶⁸ and polystyrene⁷⁴.

Below 45°C the activation energy is decreased with the increase in iodine concentration. The conductivity is enhanced considerably, which may be associated with the increase in mobility due to doping. The strong concentration dependence of conductivity of the polymer helps to interpret that transport in iodine doped PVAc films occurs via a hopping process among sites associated with the dopant molecule. A rather detailed theoretical background exists for hopping transport with a discrete activation energy. Theoretical refinements are in progress to include distribution of hopping energies and to describe alternative transport mechanisms such as multiple trapping and trap-controlled hopping¹⁶⁹⁻¹⁷³. Although these

extensions of the theoretical concept will narrow the range of possible interpretations of the transport mechanisms, a clear identification would require the experimental modification of materials parameters specific to the proposed transport model, such as the densities of hopping or trapping sites. In this respect, the concept of doping of organic polymers is extremely powerful.

3.4 Conclusions

The above discussion on electrical conduction in pure and iodine doped PVAc films enable to draw the following conclusions.

1. The transient current in PVAc decays according to t^{-n} law before reaching a steady state. The observed magnitude of n and the lack of thickness and electrode material dependence of transient current indicate carrier hopping process.
2. The absence of any significant electrode effect on current-voltage characteristics of the polymer films rules out the Schottky thermionic emission of charge carriers.
3. Thickness variation on current-voltage curve of PVAc reveals space charge build-up.
4. In low field regime Ohm's law seems to be valid in pure and iodine doped PVAc films.
5. At high field values the linearity of current with

square root of voltage for pure and doped films indicates Schottky or Poole-Frenkel mechanism. But the Poole-Frenkel mechanism is more logical because comparatively thick ($20 \mu\text{m}$) films have been used in the investigation.

6. The experimental value of Poole-Frenkel coefficient is calculated to be very low in comparison to the theoretical value. This complicates the interpretation of current-voltage characteristics in terms of Poole-Frenkel mechanism and shows a temperature dependence which is not provided in the simple model for Poole-Frenkel mechanism.
7. The value of current for pure and iodine doped films determined from the common intercept of current versus square root voltage at various temperatures agrees well with the value determined from the common intercept of current versus $\frac{10^3}{T}$ at various voltages. This shows that the field and temperature dependence of mobility in the two types of films can be described adequately according to the equation :

$$\mu = \mu_0 \exp \left[\left(-\frac{q}{kT} \right) (E^n - E_0^n) \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

The above equation is the phenomenological relationship for hopping conduction as described by Scher and Montroll.

8. Due to doping of the polymer with iodine in 10 g l^{-1} concentration, the value of current at the common intercept is enhanced to $8.6 \times 10^{-5} \text{ A}$ from $5.8 \times 10^{-6} \text{ A}$. The increase in current is associated with the increase in carrier mobility.
9. Temperature dependence of conductivity of pure and iodine incorporated films reveal that doping of the PVAc matrix with iodine enhances the conductivity of the polymer. The increase in conductivity is due to the increase in mobility of charge carriers due to impregnation of the matrix with iodine.

CHAPTER IV

Ram Adhar Shlv Adhar Stores

THERMALLY STIMULATED DISCHARGE CURRENT

4.1 Introduction

Many kinds of polymer films¹⁷⁴⁻¹⁸⁵ polarized in a high d.c. field at an elevated temperature and cooled in that field, have semi-permanent charges which exist for many years at room temperature. Depolarization currents at room temperature are frequently too small to be easily measured. To increase them one must speed up the depolarization process by heating the electret up to or above the polarization temperature. The ensuing current has been called thermally stimulated current (TSC) since it is produced by heating without an external voltage¹⁸⁶. TSC is now generally considered as particularly well suited to the study of dielectric relaxations^{187,188}. This is mainly because this technique is characterised by a very low equivalent frequency as compared to the dielectric loss method and consequently leads to a better resolution of the different relaxation processes¹⁸⁹.

As a matter of fact, the α , β relaxations arising from the conformational motions of main chain segments and from the local motions of main chain or side groups respectively are more or less superimposed at the common measurement frequencies of a hertz and thus the values of the characteristic parameters determined from the loss curves are often hybrid values¹⁹⁰. Much uncertainty results from this, and numerous discussions are found in the literature especially concerning the detailed

mechanism of the motions involved^{191,192}, the discrete or continuous nature of the possibly associated distribution of relaxation times¹⁸⁸ and the physical significance of such a distribution¹⁹². With these last problems in view, the TSC technique appears also very useful, owing to its exceptional ability for resolving multicomponent peaks by techniques such as thermal cleaning or partial polarization¹⁹³.

A wide literature¹⁹⁴⁻²⁰⁵ is available on TSC in polymers. The technique has been widely used in the study of trapping parameters in luminescent and photo-conducting materials. Lilly et al²⁰⁶ investigated TSC in mylar and teflon. Stupp and Carr²⁰⁷ suggested an ionic origin for high temperature discharge currents in poly acrylic nitrile. Guillet and Seytre²⁰⁸ conducted a detailed study of the complex relaxation modes observed in poly-L-proline. Takeda and Naito²⁰⁹ studied temperature change of dielectric constant of polystyrene using TSC measurement. TSC in corona charged polymers have been investigated by Perlman¹⁹⁹ and those in electron beam irradiated. Polymers have been investigated by Sessler²¹⁰. Ong and Turnhout¹⁸⁷ have concluded in favour of the existence of a continuous distribution of relaxation times. Recently similar conclusions have been inferred by Fischer and Rohl²¹¹ and Hino²¹² from studies on secondary peaks of polyethylene and polyethylene terephthalate respectively. Chaitan et al¹⁹⁵ however have found in polyamides that the low temperature peaks could generally be decomposed in several discrete Debye processes.

It has been shown by theoretical argument and by experiment²¹³ that only in the case of a first order kinetics polarization do the TSC peaks occur invariably at a fixed temperature. Otherwise their position is shifting in a characteristic way with changing initial polarization. In the case of a space charge release, for example, the maximum temperature is increasing with polarization temperature and polarizing time. Thus peak position data for varying polarization conditions allow one to decide in particular whether a peak is due to a first order depolarization process e.g. complex reorientation or to the release of a space charge.

TSC of polar materials²¹⁴ shows several bands or peaks. This indicates that the depolarization is realized by several different processes. Two such processes are well known, the relaxation of aligned dipoles and the relaxation of a space charge caused by mobile carriers accumulated at the electrodes. But there are still other processes which cause TSC peaks and have not yet been identified. It is one of the fundamental problems of any TSC investigation to relate the observed peaks to specific depolarization processes. TSC peak may be characterized by the maximum positions, the magnitude of the peak and the slope of initial rise of the peak. The magnitude of the peak is eventually a measure of the number of defects causing the polarization. The determination of activation is a delicate task if the peaks overlap too much, possibly no meaningful value can be obtained at all. Dependence of peak position on initial

polarization provides information on the depolarization processes.

TSC spectra are unique to the material under study. They are finger prints of them and are sensitive to impurities, additives, discharges, humidity i.e. to any chemical or morphological change. They provide a sensitive analytical tool that could be used to guide the production of materials with fixed electrical properties. TSC is an electrical spectroscopy and have practical application to electrical quality control. Recently several workers^{215,216} have used TSC technique to investigate changes produced in polymers due to doping of them with suitable impurities. Gupta and Tyagi²¹⁵ doped polyvinyl fluoride with rhodamine, alizarine, dichlorofluorescein and iodine and utilised TSC to find out the changes produced by doping. Srivastava et al have reported relaxation parameters by doping polystyrene with copper-phthalocyanine, ferrocene, anthracene, pyrene, iodine⁷⁷ and chloranil²¹⁶.

Mehendru et al²¹⁷ have reported TSC in PVAc films. They observed three TSC peaks at 53, 116 and 195°C and studied the effect of film thickness on TSC spectra of PVAc. 53°C peak was found to grow slightly with thickness. The magnitude of 116°C peak was observed to increase with film thickness and 195°C remained uninfluenced with the thickness. Total charge under all the three peaks grew linearly with the film thickness which led them to conclude uniform volume polarization in PVAc. Effect of iodine doping on TSC spectra of PVAc has been

considered by Mehendru et al²¹⁸.

This chapter reports TSC in PVAc films by varying poling temperature, bias voltage, film thickness, electrode material and heating rate and investigates the effect of iodine doping on TSC spectra of PVAc.

4.2 Theory

The instantaneous polarization of a sample which has an initial polarization P_0 can be expressed as

$$P = P_0 \exp \left(- \int \frac{dt}{\tau} \right) \quad \dots (4.1)$$

Relaxation time τ is expressed in terms of an activation energy H as

$$\tau = \tau_0 \exp \left(\frac{H}{kT} \right) \quad \dots (4.2)$$

when the sample is heated at a rate of $\beta = \frac{dT}{dt}$, the instantaneous value of depolarization current is given by¹⁸⁶,

$$J(T) = \frac{P_0}{\tau_0} \exp \left[- \frac{H}{kT} - \frac{1}{\beta \tau_0} \int_{T_0}^T \exp \left(- \frac{H}{kT} \right) dT \right] \quad \dots (4.3)$$

which shows a maximum at a temperature T_m given by

$$\tau_0 = \frac{k T_m^2}{\beta H \exp \left(\frac{H}{k T_m} \right)} \quad \dots (4.4)$$

The low temperature tail of TSC curves can be written from

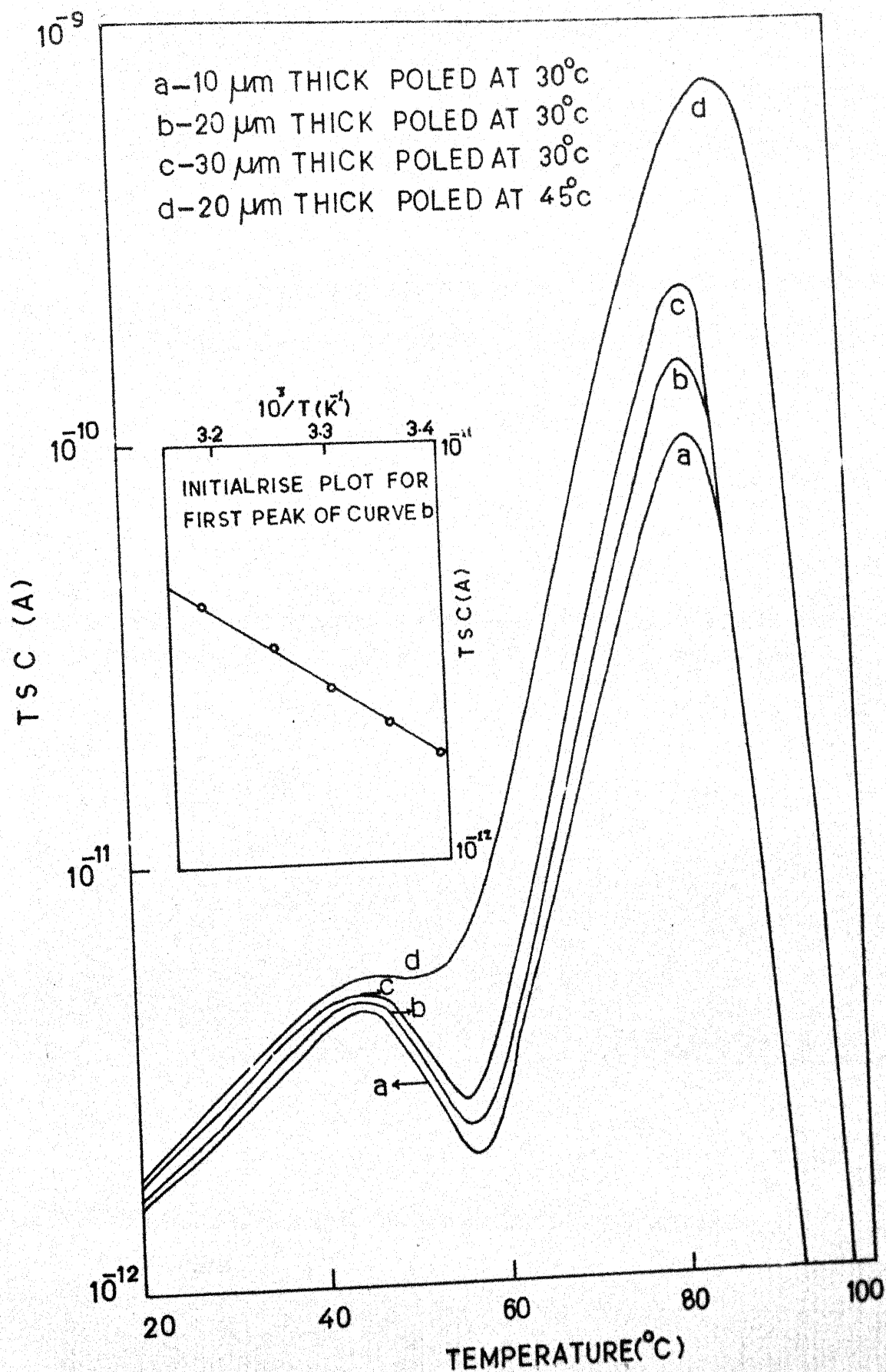


Fig. 4.1-TSC SPECTRA OF PVAc FILMS POLED BY
 4.5 kV cm^{-1} .

equation (4.3) as :

$$\log J(T) = \text{Constant} - \frac{H}{kT} \quad \dots (4.5)$$

The total charge released during heating is given by

$$Q = \int_0^{\infty} J(T) dT \quad \dots (4.6)$$

Activation energy H can be calculated from the semilog plot of $J(T)$ versus $\frac{1}{T}$ (Initial rise method of Garlick and Gibson²¹⁹) as given in equation (4.5). The relaxation times can be calculated from equations (4.2) and (4.3). One may check whether any particular experimental peak agrees with the theory by the following equation.

$$\begin{aligned} \tau(T) &= \frac{\int_{t(T)}^{\infty} J(t) dt}{J(t)} \quad \dots (4.7) \\ &= \frac{\text{Remaining charge}}{\text{Current}} \end{aligned}$$

$\tau(T)$ is determined experimentally using equation (4.7). From equation (4.2) a plot $\log \tau(T)$ versus $\frac{1}{T}$ should then be a straight line if an uniform process is operative²²⁰. The slope and intercept of this line also serve to determine H and T_0 .

4.3 Results

Fig 4.1 shows the TSC spectra of 10, 20 and 30 μm thick PVAc films. The figure also exhibits the effect of poling

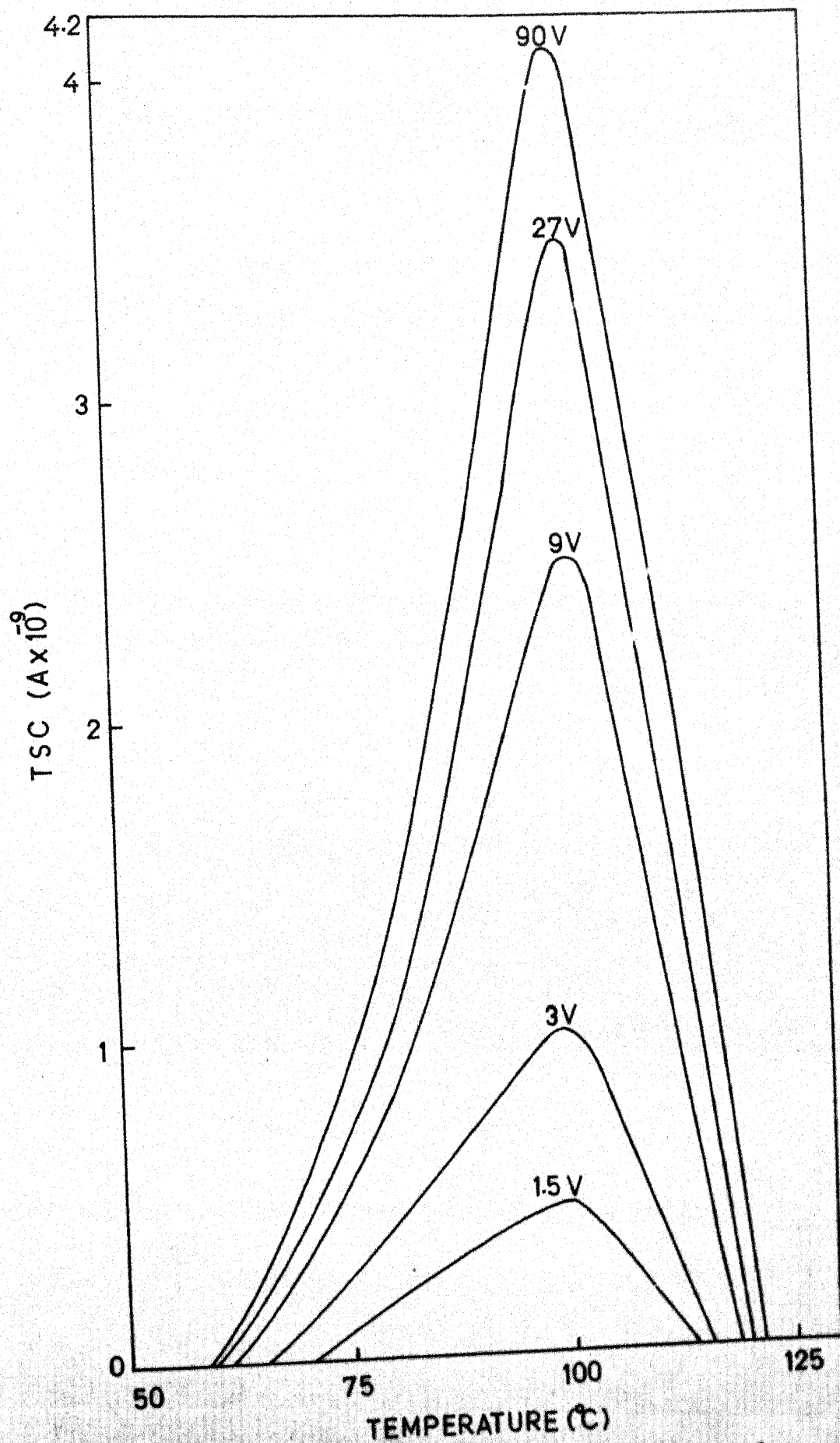


Fig. 4.2—TSC SPECTRA OF PVAc FILMS POLED AT 60°C BY DIFFERENT VOLTAGES.

temperature on TSC spectra. The curves a, b and c are the TSC spectra of films of various thicknesses poled at 30°C by 4.5 kV cm⁻¹. The spectra consist of two peaks. The first peak occurs at 45°C while the second peak arises at 83°C. There is no effect of thickness on 45°C peak while 83°C peak rises with the increase in film thickness. The positions of the peaks remain unaltered with the change in film thickness. The curve d of fig 4.1 is the TSC spectra of 20 μm thick film obtained by poling the film at 45°C. A comparison of curve b with curve d reveals that as the poling temperature is increased, the 45°C peak loses its definition. When the film is poled at 45°C, the low temperature peak becomes a shoulder. The high temperature peak is shifted to a higher temperature with the increase in poling temperature and occurs at 87°C when the film is poled at 45°C. The intensity of the high temperature peak is also increased due to increase in poling temperature. The insert in fig 4.1 is the initial rise plot²¹⁹ of 45°C peak of curve b. The activation energy of the process responsible for 45°C peak is calculated to be 0.32 eV.

The effect of electret forming field on TSC spectra of PVAc films was investigated at a poling temperature of 60°C. Films of 20 μm thickness were poled by a voltage in the range 1.5 - 90 V. The TSC thermograms are shown in fig 4.2. All the thermograms consist of a peak which arise at 100°C irrespective of biasing voltage. Increase in voltage causes the temperature where the TSC ends to shift to a higher temperature. This shows

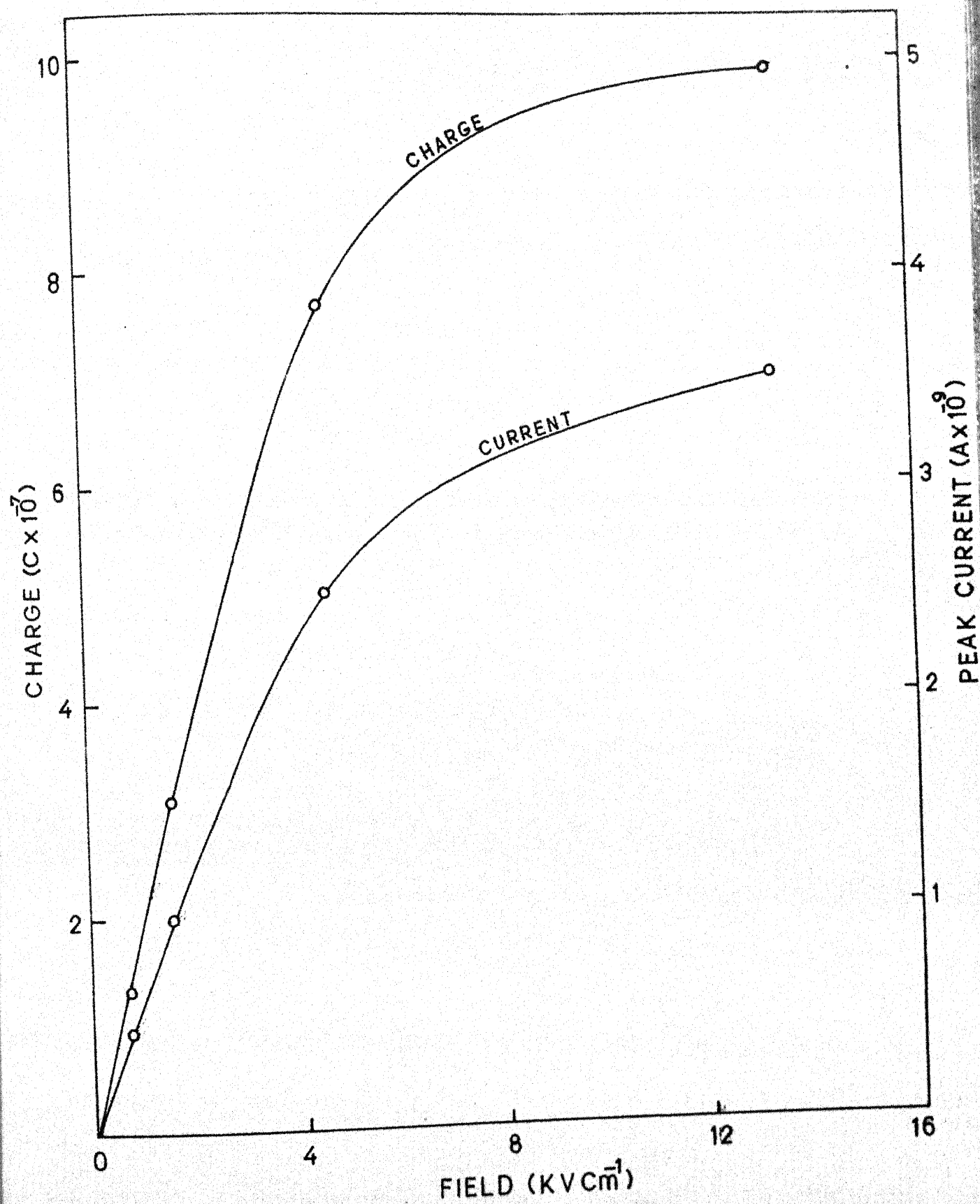


Fig. 4. 3—PEAK CURRENT AND RELEASED CHARGE VS. POLARIZING FIELD.

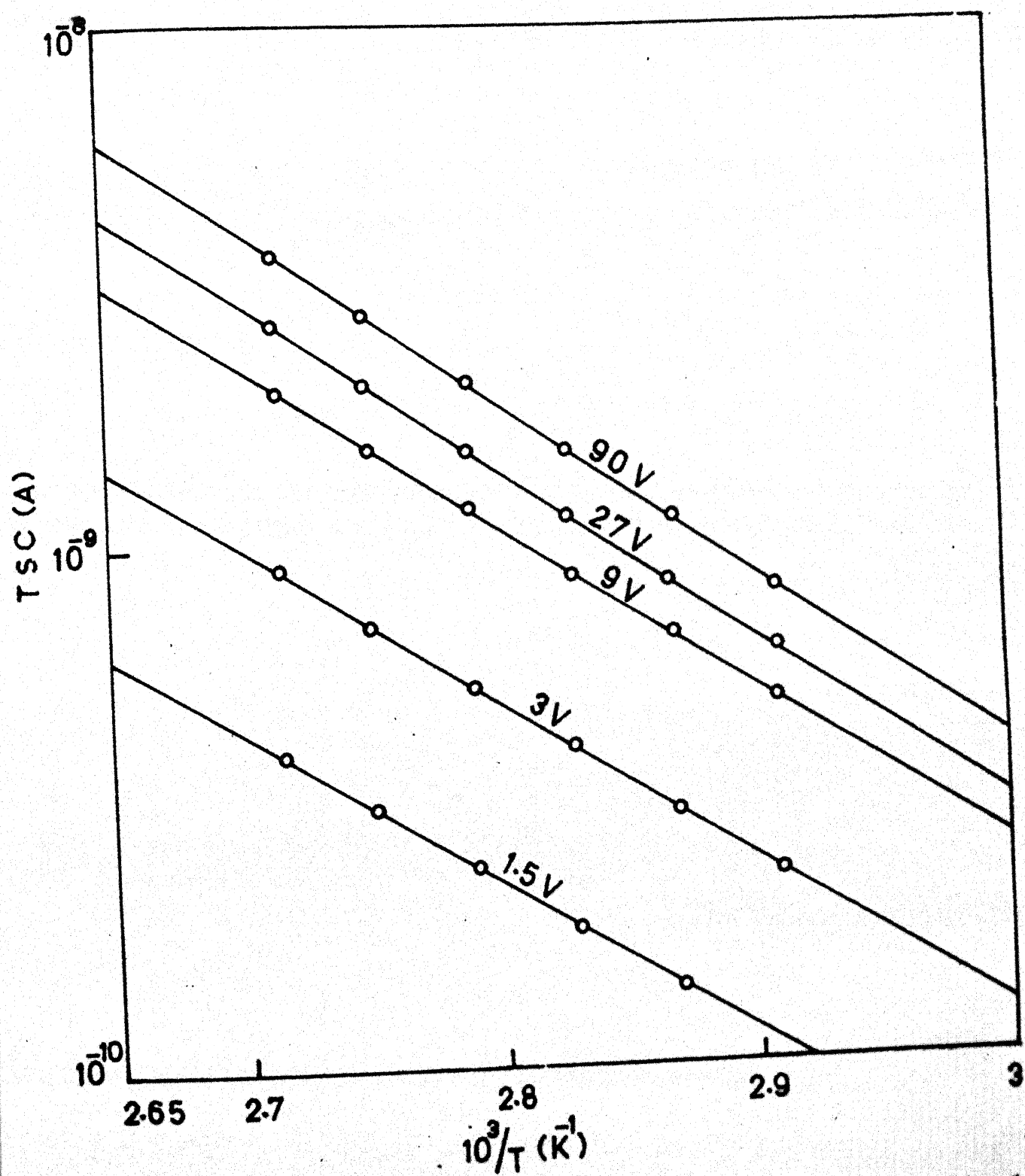


Fig.4.4—INITIAL RISE PLOTS OF TSC SPECTRA OF FIG.4.2.

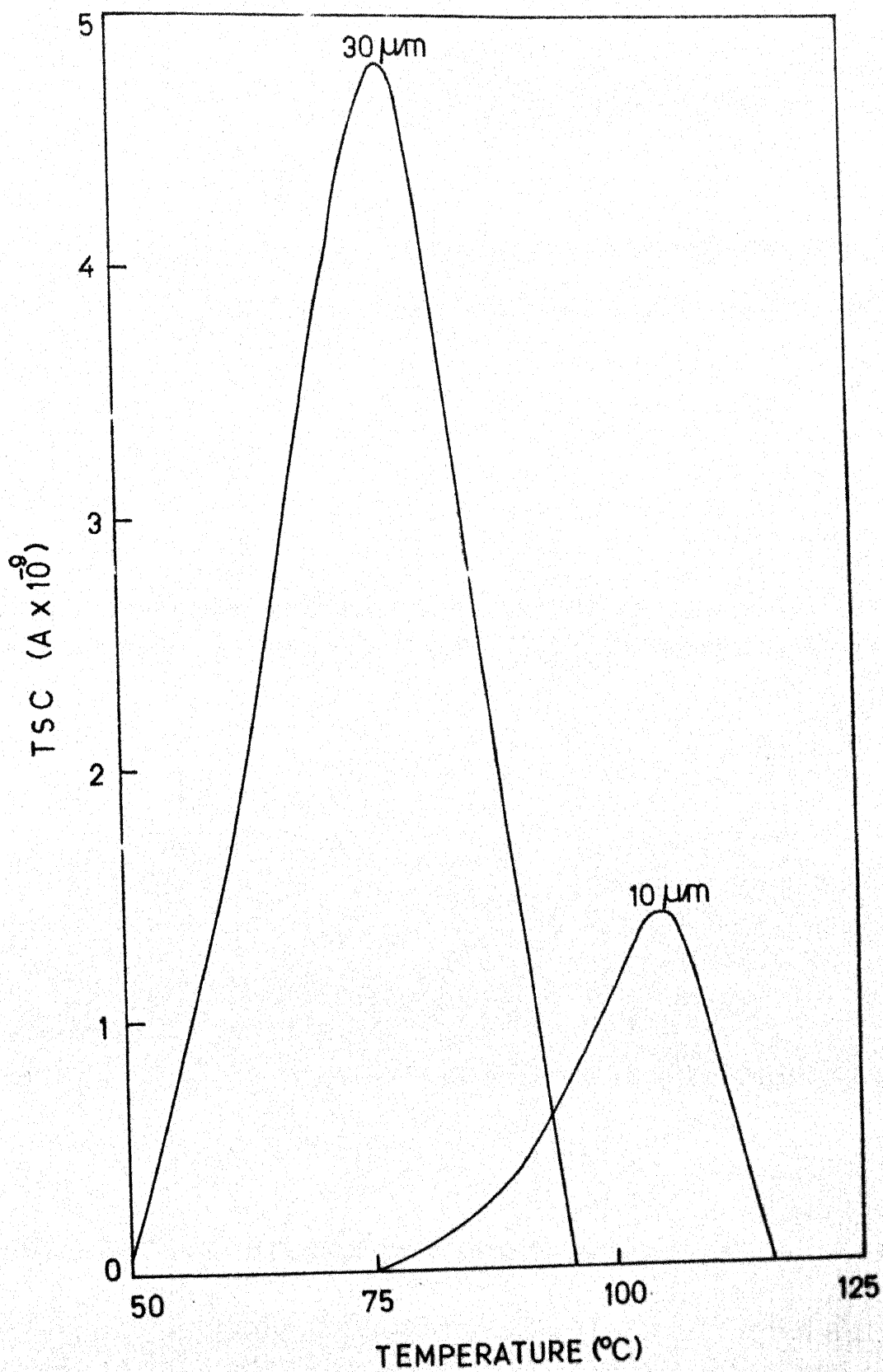


Fig. 4.5—TSC SPECTRA OF 10 AND 30 μm THICK PVAc FILMS POLED AT 60 $^{\circ}C$ BY 4.5 kV cm^{-1} .

that the electret stability is enhanced due to increase in biasing voltage. The intensity of the peak is also magnified with the increase in bias voltage. The charge released during the depolarization was estimated by integrating the current versus time curve. Peak current and charge released have been plotted against electret forming field in fig 4.3. Peak current as well as the charge released increase linearly with field upto about 4.5 kV cm^{-1} beyond which they exhibit strong saturation effect. Fig 4.4 is made of initial rise plots²¹⁹ corresponding to the TSC spectra of fig 4.2. The values of the activation energies are listed in table 4.1.

Table 4.1

Activation energy of PVAc for various bias voltages

Bias Voltage (V)	1.5	3	9	27	90
Activation Energy (eV)	0.56	0.60	0.62	0.65	0.66

Table 4.1 elucidates an increase in activation energy with the increase in biasing voltage but this increase in activation energy with voltage is larger initially than latter on.

Fig 4.5 exhibits the effect of film thickness on TSC spectra of PVAc. The films were poled at 60°C by 4.5 kV cm^{-1} . Increase in film thickness enhances the peak current and shifts the peak to occur at a lower temperature. The temperature where the TSC vanishes is also shifted to a lower temperature with the increase in film thickness. At a thickness of $10 \mu\text{m}$ the peak

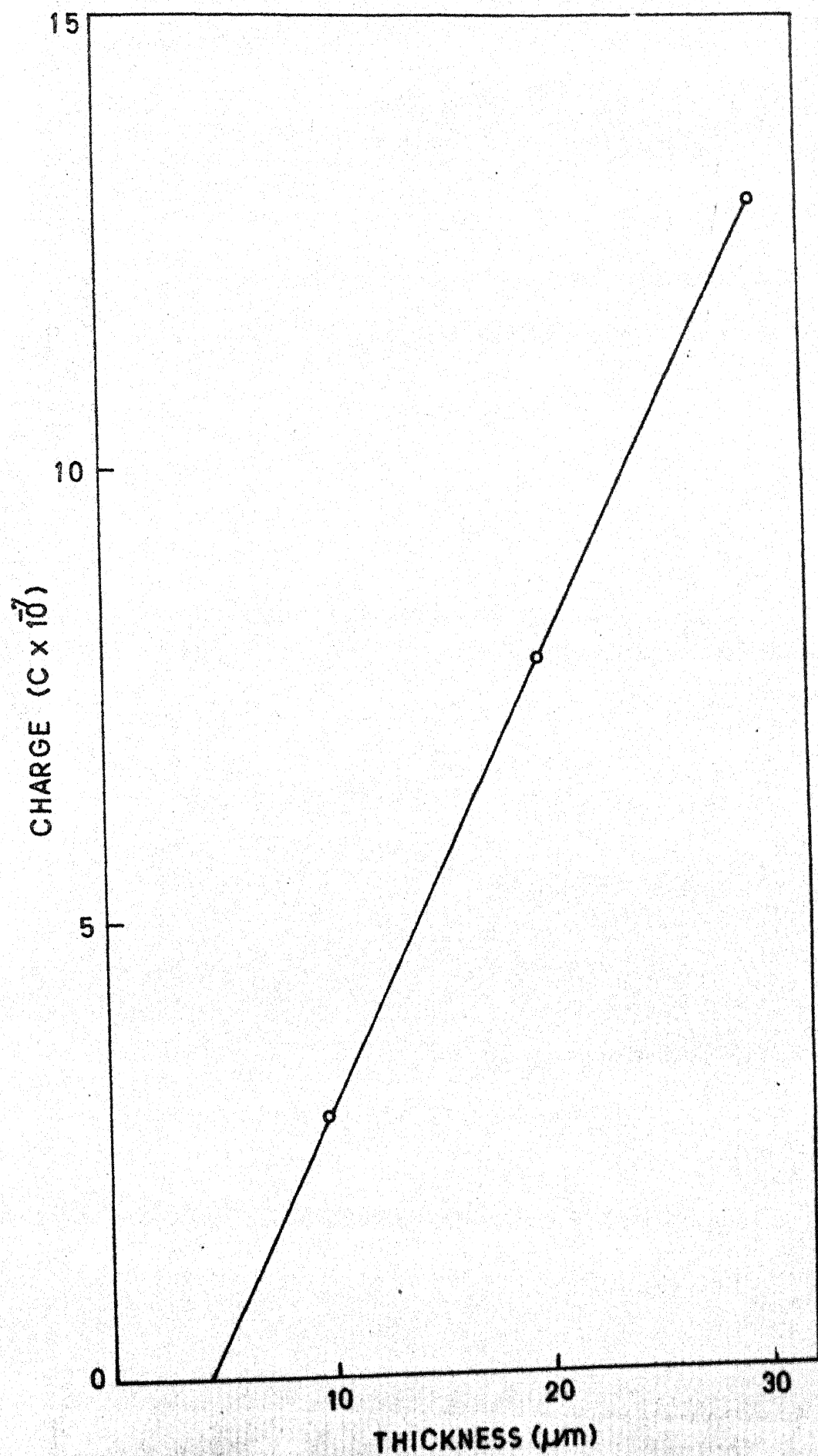


Fig. 4.6—RELEASED CHARGE VS. FILM THICKNESS.

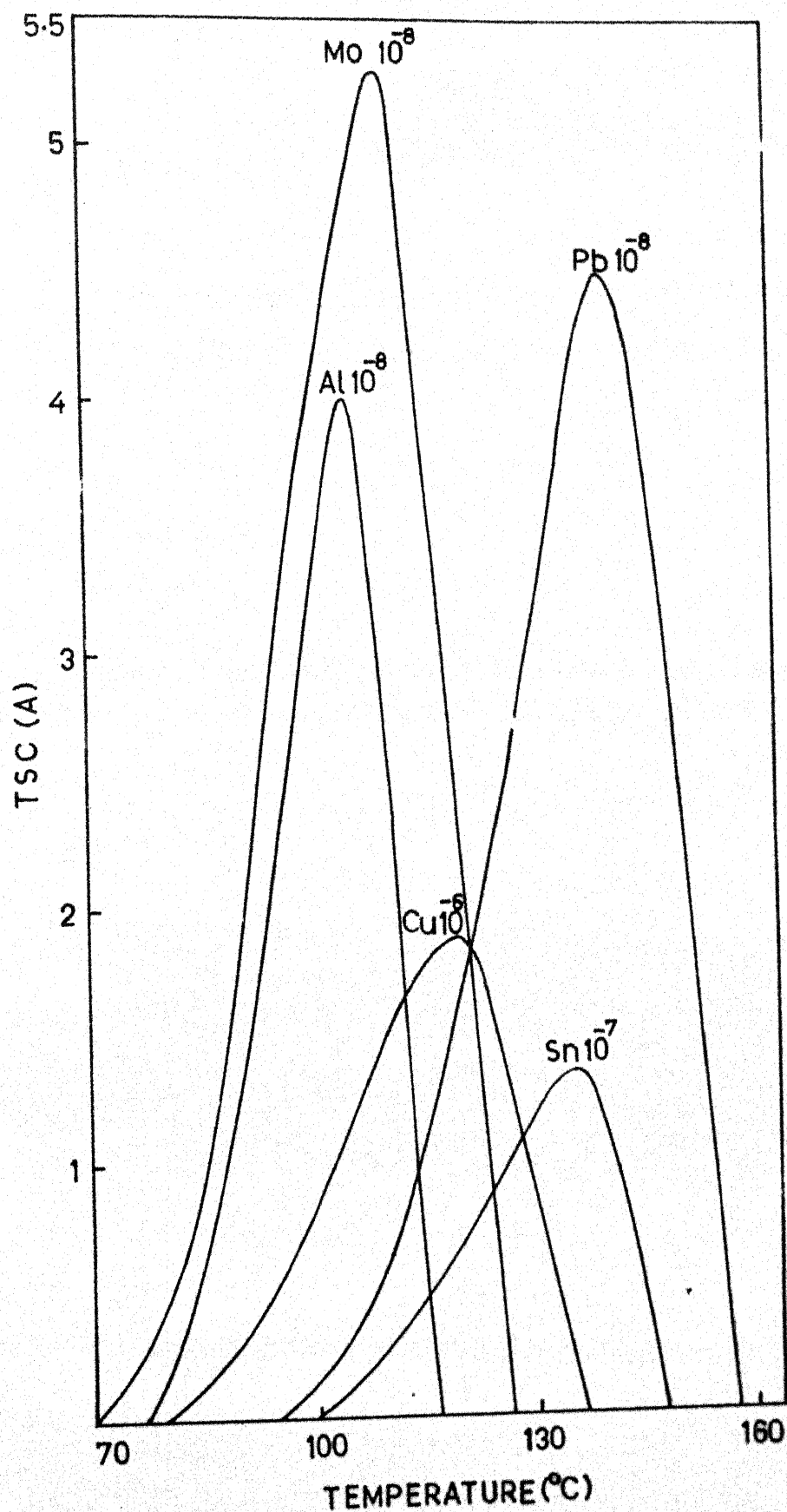


Fig. 4.7—TSC SPECTRA OF PVAc FILMS POLED AT 100°C BY 4.5 kV cm⁻¹ (CONTACT MATERIAL AND ORDER OF CURRENT ARE INDICATED ON THE CURVE).

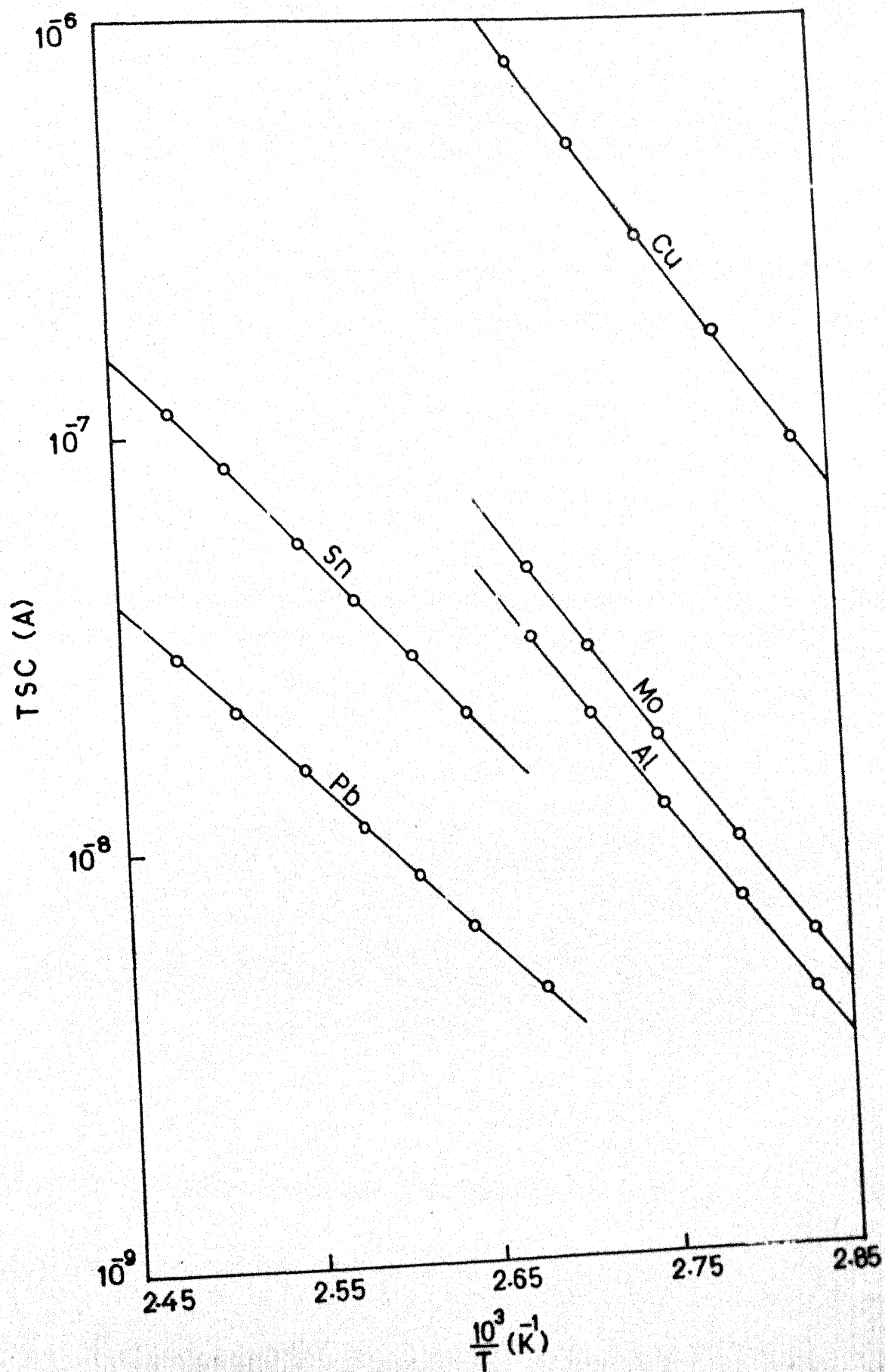


Fig. 4.8—INITIAL RISE PLOTS OF TSC SPECTRA OF Fig. 4.7.

arises at 105°C. It occurs at 100°C for 20 μm thick film (fig 4.2) while at 78°C for 30 μm thick film. Released charge versus film thickness has been plotted in fig 4.6. The plot is seen to be a straight line plot showing an increase in charge released with the film thickness but the straight line does not pass through the origin.

Electrode material effect on TSC spectra of PVAc was studied by poling 20 μm thick films at 100°C by 4.5 kV cm^{-1} . The films grown on Al, Pb, Cu, Sn and Mo substrates were employed for the purpose. The TSC spectra are shown in fig 4.7. The initial rise plots²¹⁹ corresponding to the TSC spectra of fig 4.7 have been made in fig 4.8. The TSC parameters are given in table 4.2.

Table 4.2

TSC Parameters of PVAc films in contact with different metals.

Metal	Peak temperature (°C)	Peak current (A)	Charge released (C)	Activation energy (eV)	Temperature where TSC ends (°C)
Al	105	4×10^{-8}	9.1×10^{-6}	1.14	117
Cu	120	1.9×10^{-6}	6.4×10^{-4}	1.26	137
Pb	141	4.5×10^{-8}	1.5×10^{-5}	0.87	158
Sn	136	1.35×10^{-7}	5.0×10^{-5}	0.93	148
Mo	110	5.3×10^{-8}	1.6×10^{-5}	1.21	127

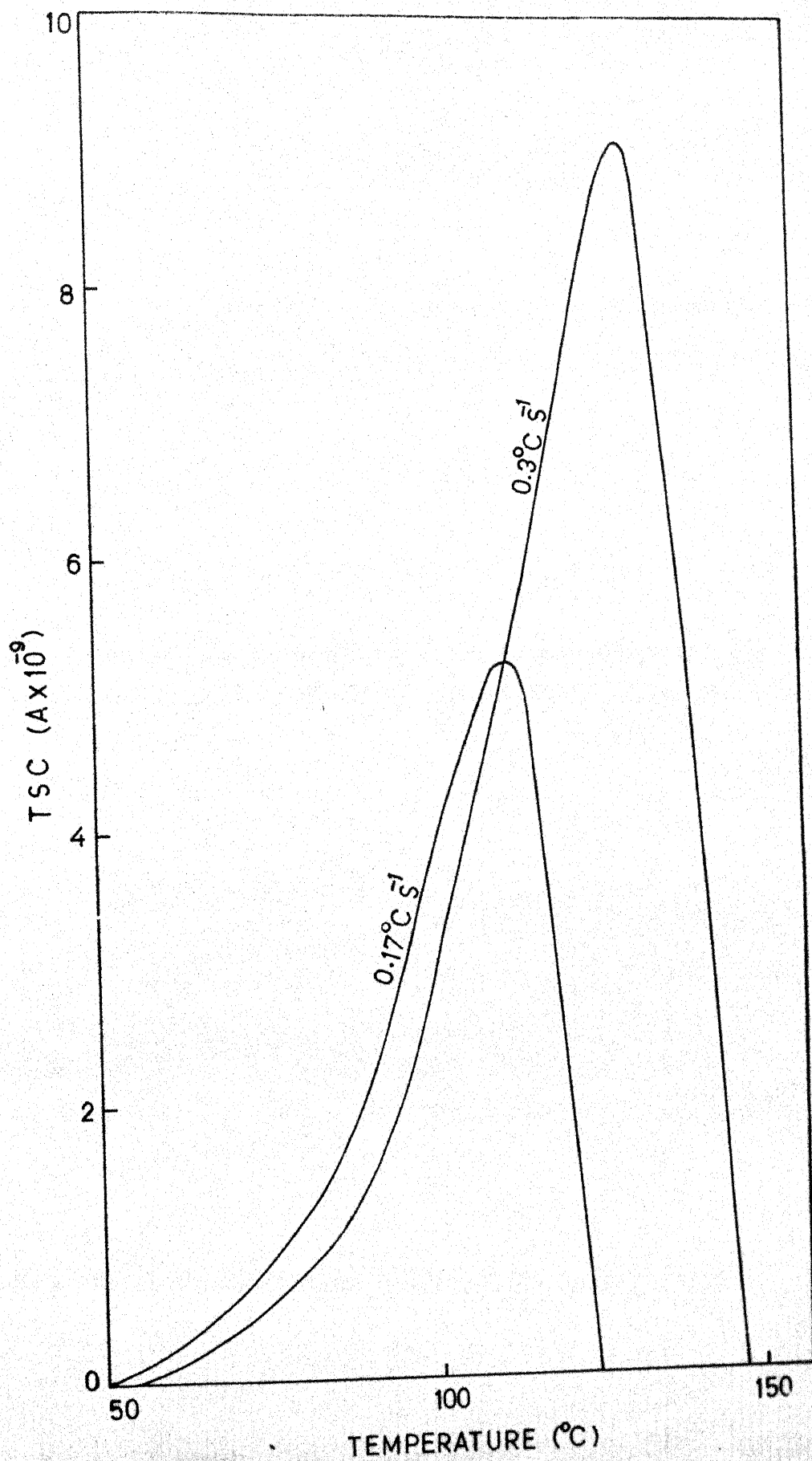


Fig. 4.9—TSC SPECTRA OF PVAc FILMS POLED AT 60°C BY 4.5 kV cm⁻¹ (HEATING RATE IS INDICATED ON THE CURVE).

With the change in electrode material, peak current, peak position, charge released, activation energy and the temperature where the TSC ends are changed. Maximum polarization in PVAc can be achieved by contacting the film with Cu.

Effect of heating rate on TSC spectra of PVAc is illustrated in fig 4.9. The films were poled at 60°C by 4.5 kV cm⁻¹ and were discharged by heating them at a uniform rates of 0.08, 0.17 and 0.30 Ks⁻¹. Fig 4.9 shows the spectra obtained at 0.17 and 0.30 Ks⁻¹ while fig 4.2 shows the one observed at 0.08 Ks⁻¹ heating rate. Increase in heating rate shifts the spectra towards the higher temperature side of the spectrum. Peak current is enhanced with the increase in heating rate and the peak arises at a higher temperature when the electret is heated at a higher heating rate. The initial rise of the current remains uninfluenced with the change in heating rate. The results are tabulated in table 4.3.

Table 4.3

Effect of heating rate on TSC spectra of PVAc.

Heating rate Ks ⁻¹	Peak temperature (°C)	Peak current (A)	Charge released (C)	Activation energy (eV)	Temperature where TSC ends (°C)
0.08	100	2.5×10^{-9}	7.7×10^{-7}	0.65	118
0.17	110	5.2×10^{-9}	8.2×10^{-7}	0.64	123
0.30	130	9.1×10^{-9}	8.8×10^{-7}	0.66	147

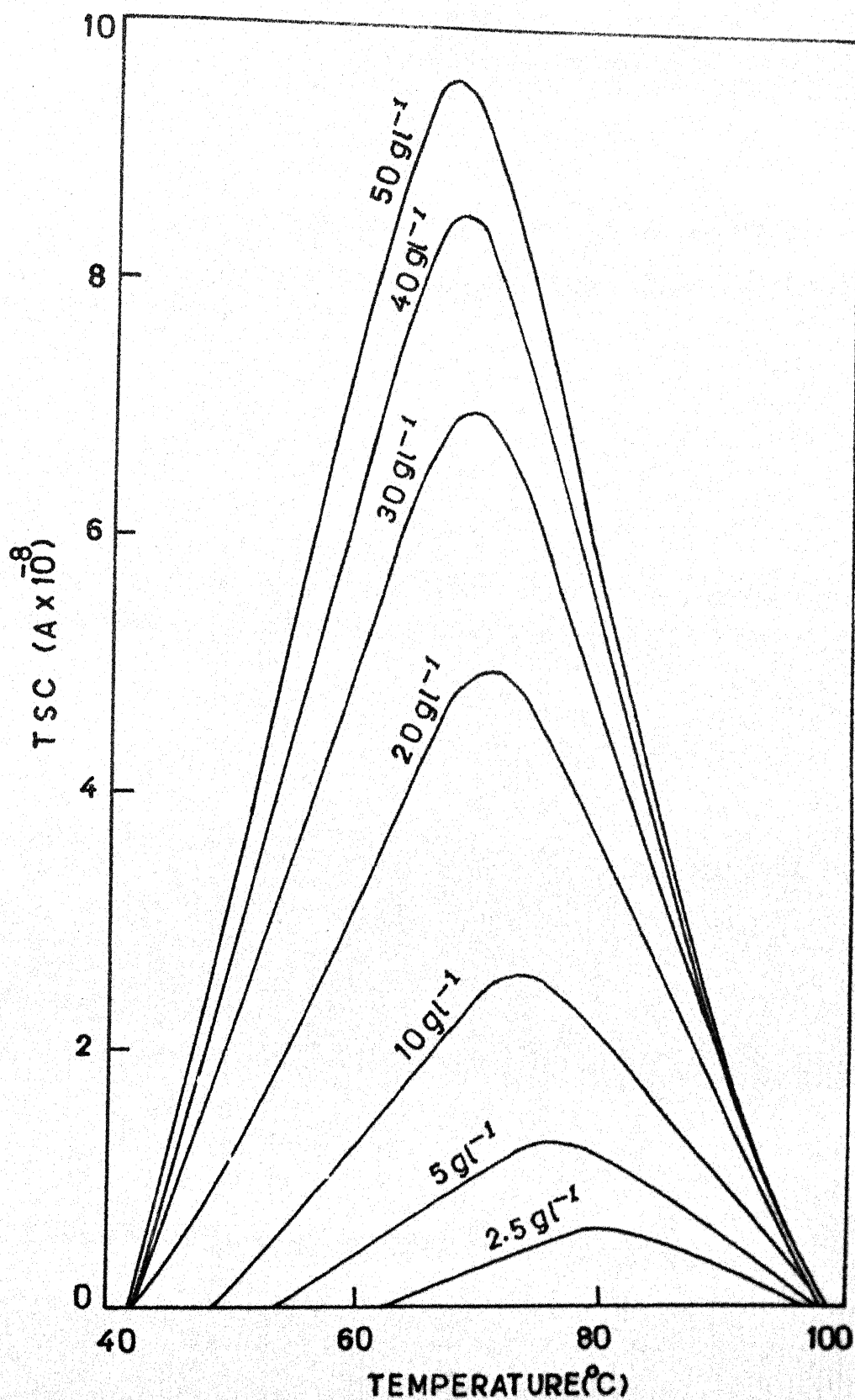


Fig. 4.10—TSC SPECTRA OF UNPOLED IODINE DOPED PVAc FILMS.

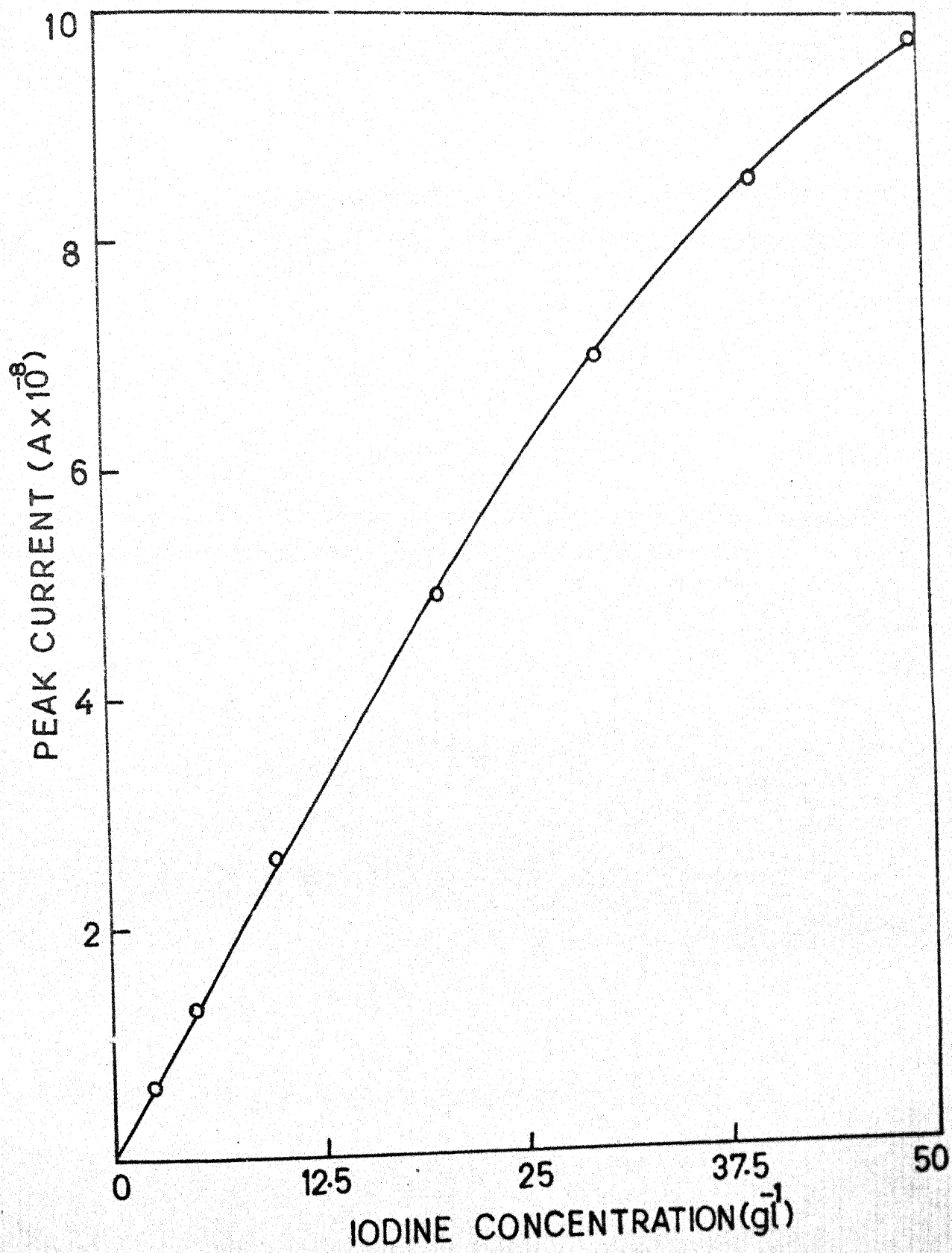


Fig. 4.11—PEAK CURRENT VS. IODINE CONCENTRATION.

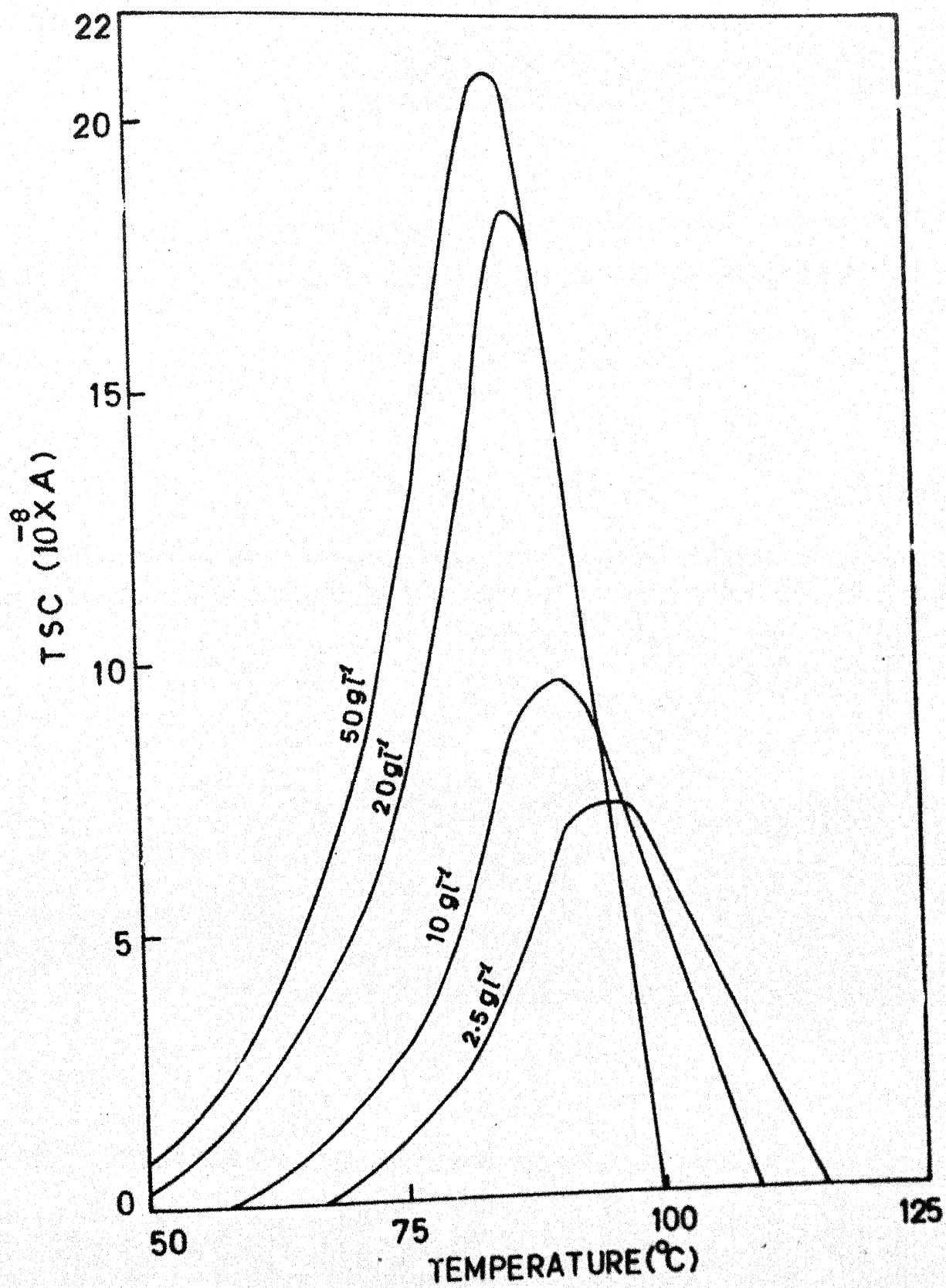


Fig. 4.12—TSC SPECTRA OF IODINE DOPED PVAc FILMS POLED AT 100°C BY 4.5 kV cm^{-1} .

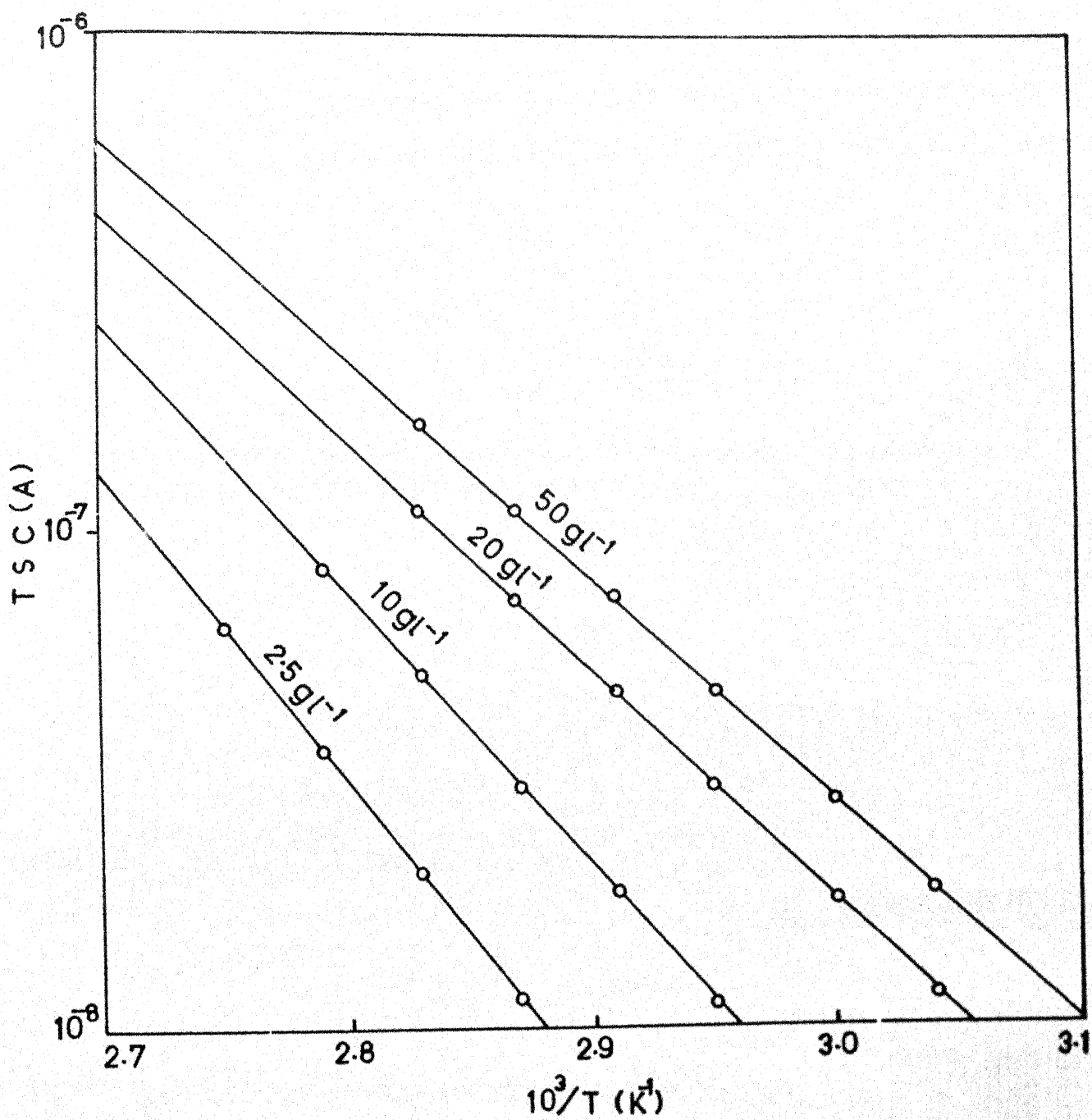


Fig. 4.13 Initial rise plots of TSC spectra of fig. 4.12

Charge stability is enhanced with the increase in heating rate. The charge released and the activation energy remain almost the same with the change in heating rate.

Prior to thermoelectric polarization, iodine doped PVAc films were found to give TSC while no such TSC was observed in pure PVAc films. Fig 4.10 shows the TSC spectra of unpoled iodine doped PVAc films incorporating iodine in the concentration range $2.5 - 50 \text{ g l}^{-1}$. The spectra of the film doped at 2.5 g l^{-1} of iodine exhibits a current maxima at 80°C . As the dopant concentration is increased, the intensity of the current maxima is enhanced followed by a slight shift in the peak temperature towards the lower temperature side of the spectrum. Peak current has been plotted against iodine concentration in fig 4.11. The plot is seen to be a straight line upto about 25 g l^{-1} beyond which a sort of saturation is seen. To study the effect of thermoelectric polarization on iodine doped PVAc films, the films doped at 2.5, 10, 20 and 50 g l^{-1} were ~~p~~^poled at 100°C by 4.5 kV cm^{-1} . The TSC spectra obtained are shown in fig 4.12. A comparison of TSC spectra of undoped and doped PVAc films under identical thermoelectric history reveals that due to doping of the polymer with iodine, the peak current is enhanced greatly and the peak temperature is shifted to a lower temperature. The peak arises at 100, 95, 90, 87 and 85°C respectively for pure and 2.5, 10, 20 and 50 g l^{-1} iodine doped films. The initial rise plots²¹⁹ of TSC spectra of fig 4.12 have been made in fig 4.13. The values of activation energies are given in table 4.4.

Table 4.4Activation energy of iodine doped PVAc films

Iodine concentration (gl^{-1})	2.5	10	20	50
Activation energy (eV)	1.24	1.12	0.91	0.87

The activation energy of pure PVAc is increased due to doping of the matrix with iodine and with the increase in iodine loading, the activation energy is decreased.

4.4 Discussion

Application of an electric field always produces a small movement of charges within the atoms of a dielectric, displacing the negative electronic cloud relative to the positive nucleus and thus temporarily generating a small dipole moment and a consequent atomic or deformation polarization. This effect occurs within very short times, its time scale can not be changed from outside. Thus its influence on the persistent polarization of the electret can be disregarded. Many dielectrics, including polymers, contain molecules that have an electric moment. An applied field tends to align these elementary dipoles along its own direction and thus produces an electric moment of the whole body giving rise to dipole polarization, essentially a volume effect.

All dielectrics contain a small number of free charge carriers, ions or electrons or both. An electric field

tends to separate positive from negative charges and to move them toward the electrode. The structure of many polymers is not homogeneous, there exist microscopic domains or grains separated by highly resistive interfaces. In this case the charge carriers can move relatively freely only within single grains, piling up along the barriers which they are unable to surmount as they lack the necessary energy. Alternatively, when the dielectric contains many irregularly distributed traps with widely different well depths, carriers might move in the direction of the field until they fall into deep traps from which they do not have enough energy to escape unless reactivated by a temperature increase. Both these interfacial polarization effects constitute again a volume polarization.

Ionic conduction currents in homogeneous dielectrics usually lead to the formation of space charge clouds in the electrode regions. The effect results in a macroscopic space charge polarization of the dielectric.

The sources of the internal polarization described so far have been charges originating from and remaining within the dielectric, but a polarization can also be caused by the deposition or injection of charge carriers from outside. Deposition of equal and opposite charges on opposing surfaces of a dielectric produces an external polarization. The distinction between internal and external polarization is due to Mikola²²¹. Charges can also be shot into the dielectric using penetrating electron beams. Such electron charged dielectrics now are also

called electrets, a rather loose use of the term.

The degree of polarization and its rate of decay depend on the nature of the dielectric and the experimental conditions, in particular the temperature. A dielectric becomes an electret when the rate of decay can be slowed down so much that a significant fraction of the field induced polarization is preserved long after the polarizing field has been removed.

Dipole orientation is strongly temperature dependent; at high temperature the forces opposing rotation are lessened. Thus a high degree of polarization can be achieved in a short time by application of an electric field at a high temperature. If the dielectric is cooled and the field removed only after a low temperature has again been reached, dipoles return to the original disordered state very slowly because rotation is hindered by strong viscous forces. The polarization is thus frozen-in. A similar behaviour is found in the case of space charge and interfacial polarization. The mobility of charge carriers is very low at room temperature, but increases strongly with temperature. Thus the previous reasoning applies here too. Space charge clouds and charges accumulated along interfaces can be frozen-in.

All types of internal polarization lead to surface charges which have the opposite polarity to that of the corresponding polarizing electrodes. Therefore heterocharge formation should be, and is, a very general effect. Every decrease of the internal polarization due to rotation of dipoles or recombination

of ions within the dielectric frees image charges which flow back through the external circuit where a discharge current is recorded. Analogously every increase of polarization gives a charging current. Therefore build-up and dissipation of internal polarization can be investigated by means of current measurement. Current peaks are observed at temperatures where dipole orientation or carrier release from traps is activated.

The processes taking place during discharge are similar to those occurring during charging. Generally speaking, they only behave in an opposite way. The net charge of an electret usually arises from aligned dipoles and space charges. The latter are excess charges which cause the electret to be not locally neutral. However, before the electret formation the neutral polymer already contained free charges, they manifest themselves in a conduction current when a field is applied. So in addition to the excess charges there are free equilibrium charges in the electret. These do not contribute to its net charge, but are responsible for its ohmic conductivity. In heteroelectrets the excess charges are intrinsic and bipolar. They originate from those charges that first take part in conduction and were accumulated near the electrodes during formation. This field motion is opposed by diffusion. Moreover during their transport a part of the charges is lost by recombination with opposite carriers.

The decay of the charge of an electret during TSC results from dipole reorientation, excess charge motion and

ohmic conduction. The first process will be clear, the thermal agitation will reorient the aligned dipoles at random. The motion of excess charges originates from space charge limited drift and diffusion. The first motion is due to the local electric fields forcing the mobilized excess charges to drift towards opposite charges, where by electric neutrality is restored. The excess charges will eventually recombine either with their opposed image charges or with opposite excess charges within the polymer. Whichever is the case, their gross motion should generate a discharge current opposed to the charging current¹⁰⁶.

The temperature dependence of the dipole reorientation can be differed from the motion of excess charges. The latter will conform closely to that of ohmic conduction, from which the charges often originate. In particular, we may expect the current maxima for dipole reorientation to occur at lower temperature than that of the excess charge motion. The first process requires only a rotational motion of molecular groups, whereas the latter process involves a motion of molecular groups (ions) over macroscopic distances. The activation energy predicted theoretically by Reddish²²² for the relaxation process resulting from the local twisting of the main chain or the orientation of the side groups in a polymer is about 0.2 eV. Considering the value 0.32 eV of activation energy obtained for 45°C peak and the observation that the magnitude of this peak does not depend upon film thickness (fig 4.1), the relaxation

process associated with this peak is the orientation of the side groups and or local twisting of the main chain. It is difficult, however, to differentiate whether the low temperature relaxation in PVAc is due to the local twisting of the main chain only or it is also due to the motion of the side groups in the polymer chain.

When PVAc film is poled at 60°C, the low temperature peak loses its definition and only a single peak at 100°C is observed in the thermogram. The dipolar contribution calculated from Debye's equation does not respond to the high value of charge released. To account for the charge released probably the displacement of charges during polarization with their subsequent trapping is also responsible¹⁷. The charges may also be injected from electrodes into the polymer film. It is only at temperatures above the glass transition of the polymer that the molecular chains are sufficiently agitated to release the charges stored in them. Comparatively high conductivity may also play a role here.

4.4 (a) Field Dependence of Polarization

By varying electric field, one may distinguish between dipolar peaks and space charge peaks¹⁹⁶. The former increase linearly with field, the latter nonlinearly. However, the deviations from linearity will not be very large. Peak current and charge released vary linearly with applied field upto about 4.5 kV cm⁻¹ and then they exhibit saturation with

field (fig 4.3). Increase in biasing voltage has an effect of increasing the activation energy (table 4.1). These results show that the peak arises due to displacement of charges through microscopic distances. Gerson and Rohrbough¹⁷ have suggested that in some dielectric mechanisms charges suffer microscopic displacements during polarization and become trapped when the specimen is heated, these charges are released and recaptured. This process shows a similar field dependence to that predicted for dipolar motion. The value of activation energy is close to the values expected on the basis of ionic traps²²³.

4.4 (b) Temperature Dependence of Polarization

By varying the poling temperature, one can detect that a heteroelectret contains a distributed dipole polarization or not. For a single dipole relaxation the current is lowered as poling temperature is lowered, but the position of its maxima will remain the same. For a distributed polarization maxima will shift¹⁰⁶. When poling temperature is low, only the fast sub-polarizations will be filled and the TSC will be cut off on the high temperature side, because of the unactivated slow polarizations. When poling temperature is raised more sub-polarizations are activated and the current maxima will rise and simultaneously shift to a higher temperature. When all the sub-polarizations are filled the current maxima appear at the transition temperature.

For homoelectrets poling temperature mainly influences the penetration depth of the injected carriers²¹³. Penetration depth is increased with the increase in temperature. By changing the polarity of injection voltage, negative or positive carriers can be injected which can have different drift mobilities, retrapping and recombination rates. Decay of positive carriers is faster than negative carriers. Only the negative carriers, and not the positive ones can be injected at room temperature. This makes it likely that electrons contribute significantly in a negative injection. At low temperature the conductivity is low and the fewer carriers are available to accumulate, this weakens the space charge peak. If its position is not changed it means that the carriers are not trapped at different energy levels.

When PVAc film is poled at 30°C, two TSC peaks at 45 and 83°C are obtained. Low temperature peak joins with the high temperature peak when the film is poled at 45°C. For poling temperatures 60 and 100°C, the peak arises at 100 and 105°C respectively. The position of the peak shifts with poling temperature and this shift in peak temperature with poling temperature saturates. The values of activation energy for poling temperatures 60 and 100°C are calculated to be 0.62 and 1.14 eV respectively. Thus activation energy increases with the increase in poling temperature. This fact, combined with the magnitude of activation energy associated with the peak, leads to conclude that the trapping site itself is being destroyed due to increased molecular motion²²⁴.

4.4 (c) Thickness Dependence of Polarization

Charge released is observed to increase with the thickness (fig 4.6). This is so because thicker film accumulates more space charge. A uniform volume polarization seems to be operative. However, the peak position is altered with the change in film thickness. For thicker film the peak arises at a lower temperature.

4.4 (d) Electrode Material Effect

Variation in electrode material exhibits pronounced changes in TSC spectra of PVAc films, (fig 4.7 and table 4.2). Dipolar peaks remain uninfluenced by the choice of electrode material¹⁰⁶ which is contrary to the present observation ruling out dipole reorientation. The interpretation of depolarization appears to be reasonably possible in terms of charge detrapping of a space charge built-up due to carriers injected from the electrodes. The charges are injected from the electrodes into the polymer film and are then trapped. It is only at temperatures above the glass-transition of PVAc that the molecular chains are sufficiently agitated to release the charges. The amount and the sign of charge injected depend on the relative work function of the metal-polymer interface. The various metal-polymer interfaces possess different charge exchange rates which change the space charge storage and the current released by diffusion. The first stage of charging is carrier injection and the second stage is the entrapment of these charges in the border layer.

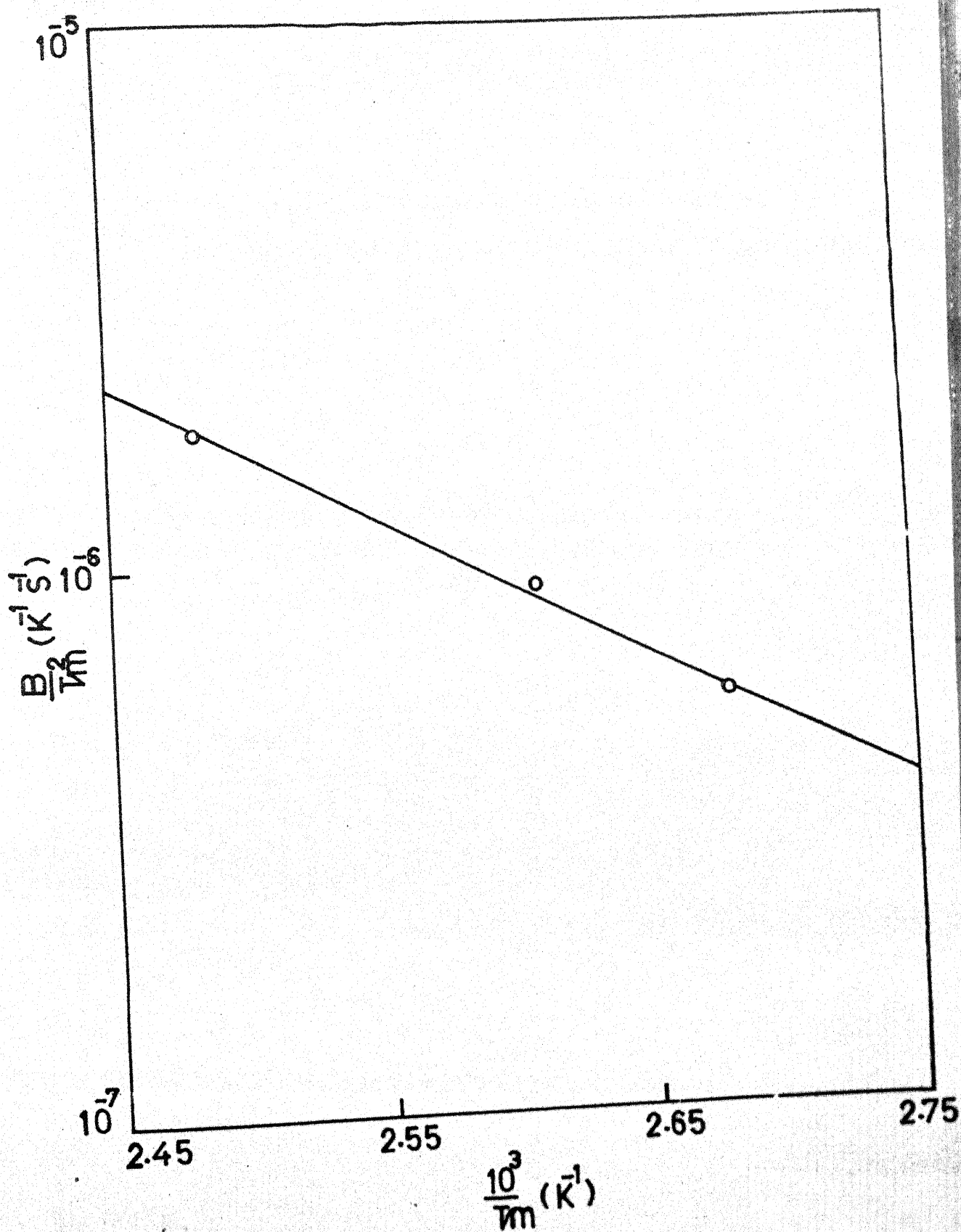


Fig. 4.14 — B/T_m^2 VS. $10^3/T_m$

4.4 (e) Effect of Heating Rate

Important experimental parameter is heating rate. This affects the height and the position of the thermogram¹⁰⁶. The current peak increases and broadens with heating rate (fig 4.9 and table 4.3). This is so because if the heating rate is higher, the same charge has to be released in a shorter time. It is only the initial slope which remains the same. Current maxima varies almost proportionally to the heating rate. At the same time it shifts to a higher temperature because the polymer responds less quickly to a higher heating rate. One can calculate activation energy by noting the shift in peak position with varying heating rate. The equation (4.4) can be rewritten in the form :

$$\frac{\beta}{T_m^2} = \frac{k}{H T_0} \exp \left(- \frac{H}{k T_m} \right)$$

$$\text{or } \log \frac{\beta}{T_m^2} = \text{Constant} - \frac{H}{k T_m}$$

In fig 4.14, $\log \frac{\beta}{T_m^2}$ has been plotted against $10^3/T_m$. The plot is a straight line. The value of activation energy is calculated to be 0.52 eV. This value does not agree with the value determined from initial rise method.

4.4 (f) Unpoled TSC from Iodine Doped Films

On heating, virgin iodine doped films reveal a

current maxima at 80°C (fig 4.10). Turnhout¹⁰⁶ has observed this effect in several polymers and has explained that the peak occurs due to the thermal dissipation of the so called moulding charges created during the film preparation. Such a preheating is necessary to remove the stray charges which might effect TSC thermograms. Unpoled PVAc films do not give any TSC on heating before thermoelectric treatment. Pure as well as the doped films have been prepared by the same technique. Hence the TSC does not occur due to moulding charges. Several workers²¹⁸ have pointed out formation of charge transfer (CT) complexes due to doping of polymers with iodine. Recently Tiwari et al⁷⁵ report unpoled TSC in polystyrene by doping it with iodine. Iodine forms CT complexes with PVAc and so the doped films give TSC prior to thermoelectric polarization. This view is also clear because pure PVAc films do not give any TSC on heating. More and more CT complexes are formed due to increase in iodine concentration. Consequently peak current increases with iodine concentration (fig 4.11).

4.4 (g) Effect of Doping on Polarization

Fig 4.12 exhibits the effect of iodine loading on TSC spectra of PVAc films. Due to doping the intensity of current maxima is greatly modified because iodine forms CT complexes with the polymer. The presence of iodine facilitates polymer chain motion and hence the TSC peak occurs at a lower temperature. Iodine creates new trapping sites and the doped

films store more space charges. Space charge peaks are intimately related to conduction mechanism. The charges may be electronic or ionic and may originate from dissociation of impurity molecule. For space charge polarization there must be one type of charges having higher carrier mobility. Increase in iodine concentration enhances peak current and diminishes activation energy (table 4.4). Decrease in activation energy may be associated with the increase in carrier mobility⁷⁵.

4.5 Conclusions

TSC study of pure and iodine doped films enables to draw the following conclusions.

- (1) The low temperature relaxation of 45°C in PVAc occurs due to orientation of the side groups and or local twisting of the main chain. It loses its definition under certain conditions of polarization.
- (2) Field and thickness dependence of polarization reveal uniform process to be operative for high temperature relaxation of PVAc.
- (3) Shift in peak position with poling temperature shows that the charges are trapped at various trap depths.
- (4) Marked electrode dependence of TSC spectra exhibits carrier injection mechanism.

- (5) The results observed by varying the heating rate do not favour dipole reorientation mechanism.
- (6) Unpoled TSC from iodine doped films is attributed to the formation of CT complexes due to doping of the polymer with iodine.
- (7) Dependence of polarization on iodine concentration and the decrease in activation energy with increasing iodine loading indicate that carrier mobility is greatly enhanced due to impregnation of the matrix with iodine.

CHAPTER V

Ram Adhar Shiv Adhar Stores

PHOTO DEPOLARIZATION CURRENT

5.1 Introduction

Many polymers²²⁵⁻²²⁸ show polarization effects when an electric field is applied in the presence of illumination. It is a problem of interest from the stand point of the technology involved in using these materials in radiation environments and for the pieces of information it gives on conduction processes in insulating materials. The processes taking place during photopolarization and depolarization are the basis of persistent electrical photography²²⁵. Persistent internal polarization is a striking static phenomenon and supplies several important pieces of information which can not be easily obtained otherwise.

The studies have been made of the spectral characteristics and photoelectric sensitivity of many organic polymers²²⁹⁻²³⁵. In spite of the considerable number of papers devoted to photoelectric sensitivity, so far there has been no sufficiently well founded theory of the mechanism of photoexcitation of current carriers and their transfer in polymeric structures. Nevertheless the characteristics of photo-conduction of several polymers give grounds for considering these materials as promising substances for practical use. There are no experimental results available for polymeric semiconductors that could fully explain the processes of photo-conduction. Such results have been obtained for low molecular weight semiconductors²³⁶⁻²³⁹.

There have been a number of recent studies of photoconduction induced in polymers with ultraviolet light. The most extensive investigation has been carried out on low density polyethylene for which it has been established that hole injection occurs from the anode. This observation by Vermeulen, Wintle and Nicodema²⁴⁰ has been confirmed by Comins and Wintle²⁴¹ and by Mizatani²⁴² who showed that the hole injection regime is dominant only when the applied field is below 300 kV cm^{-1} . The photo current varies linearly with illumination intensity²⁴¹ and with voltage²⁴². It exhibits no dependence upon the thickness of the specimen at constant voltage, indicating that the current is controlled by the contacts²⁴¹, thus confirming an earlier suggestion by Wintle. It has been proposed by Wintle²⁴³ and Tibensky²⁴⁴ that the photo injected charges traverse the full thickness of the specimen and are not permanently trapped because the illumination fulfills the subsidiary role of injecting any charges which may be trapped in the bulk. These authors also showed that the dark absorption currents and the photocurrents were independent of one another and supported these observations with rough numerical estimates of the magnitude of the charge of each type in a typical experiment.

Hersping et al²⁴⁵ have reported that polyvinyl chloride films exhibit a sensitive photo-conduction under the illumination of UV light. About the same time, however, Kryzewski et al²⁴⁶ have observed the decrease of conductivity of polyvinyl chloride films under UV illumination, namely a

negative photo-conduction. Mizutani et al²⁴⁷ investigated photo-conduction of poly vinyl chloride in more detail and concluded that photo-conduction in the polymer is induced not only by UV light but also by visible and near infrared light unlike polyethylene in which photo-conduction is induced mainly by UV light.

Takai et al²⁴⁹ have developed an experimental technique to confirm the photo-injection from metal electrodes and to determine the sign of the injected carriers and have applied it to polyethylene terephthalate in the wavelength region 400 nm to 320 nm. The dominant carriers injected are electrons for aluminium and copper and electrons and holes for silver at round 370 and 340 nm respectively, but for the others they can not be determined due to the small photo injection currents. These photo injection processes are mainly controlled by the work functions of metals and insulators, but can not be explained by the work function only and the surface states are tentatively proposed. Photo-emission of electrons from metallic electrodes into poly N vinylcarbazole and the threshold values of internal photo-emission change according to the work function of the metal have been investigated.

Recently there have been a few reports on photo-polarization of doped polymer films^{250,251}. Shrivastava et al²⁵⁰ study electrode effect on photo-polarisation of copper phthalocyanine doped polystyrene films and investigate build-up of polarisation²⁵¹ with field and time. These results on photo-

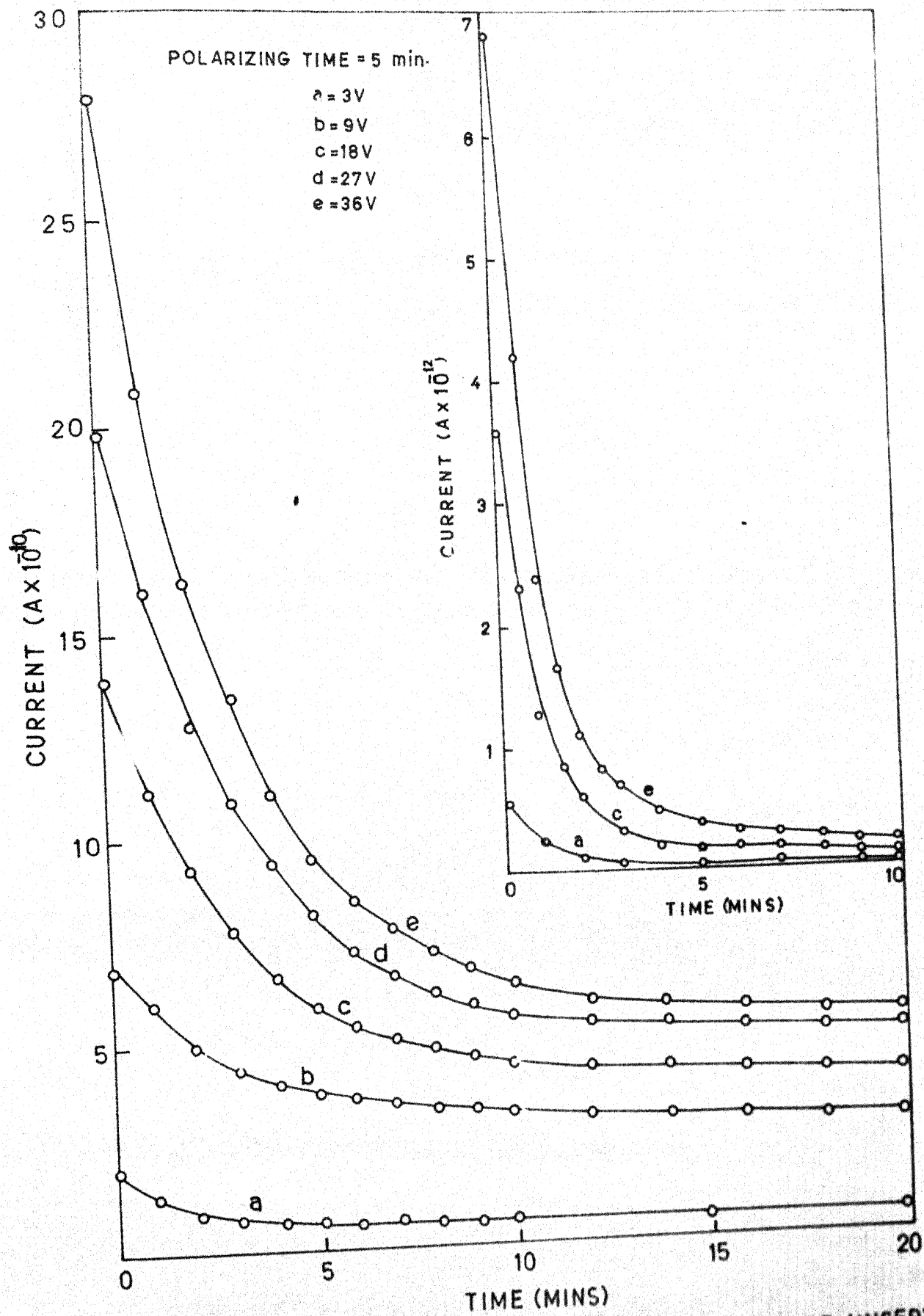


Fig. 5. 1—DEPOLARIZATION CURRENT DECAY MODE OF PURE (INSERT) AND 5g l⁻¹ IODINE DOPED PVAc FILMS AT VARIOUS VOLTAGES.

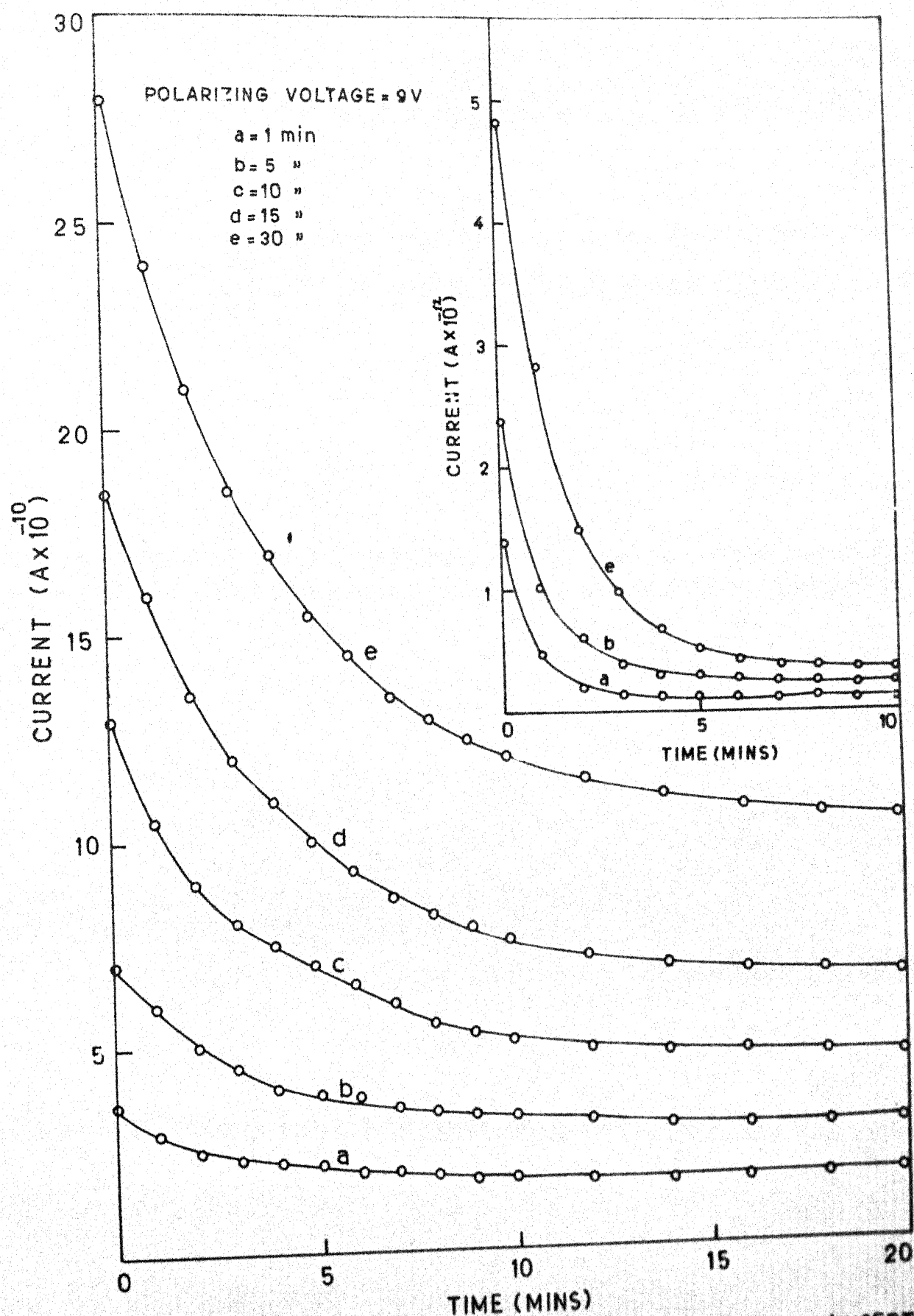


Fig. 5.2-DEPOLARIZATION CURRENT DECAY MODE OF PURE (INSERT) AND 5 g l⁻¹ IODINE DOPED PVAc FILMS AT VARIOUS POLARIZING TIMES.

polarisation of doped polymers show that life time of photo-generated carriers can be greatly modified by doping the polymers with suitable impurities.

This chapter reports photodepolarisation currents in pure and iodine doped PVAc films and investigate the build-up of polarisation with field and time. The electrode effect on photodepolarisation current is also reported in two types of films.

5.2 Results

To study the build up of polarisation with field, films were poled by 3, 9, 18, 27 and 36 V in 5 min. and were depolarised by UV radiation. Fig 5.1 exhibits decay mode of depolarisation current for 5 gl^{-1} iodine doped PVAc films while the insert shows current versus time for pure PVAc photoelectrets. Hundred times more depolarisation currents are released from doped films. Initially the current decays rapidly and then slowly to reach the steady value. Steady state in PVAc films is attained sooner than in iodine doped films. Photoelectrets fabricated in 1, 5, 10, 15 and 30 mins by 9 V were depolarised to understand the build up of polarisation with time. Fig 5.2 describes the decay modes of depolarisation current for 5 gl^{-1} iodine doped PVAc films while the insert is made of current versus time curves for pure films. The initial and final values of depolarisation currents depend on polarising time. The value of charge released during the depolarisation

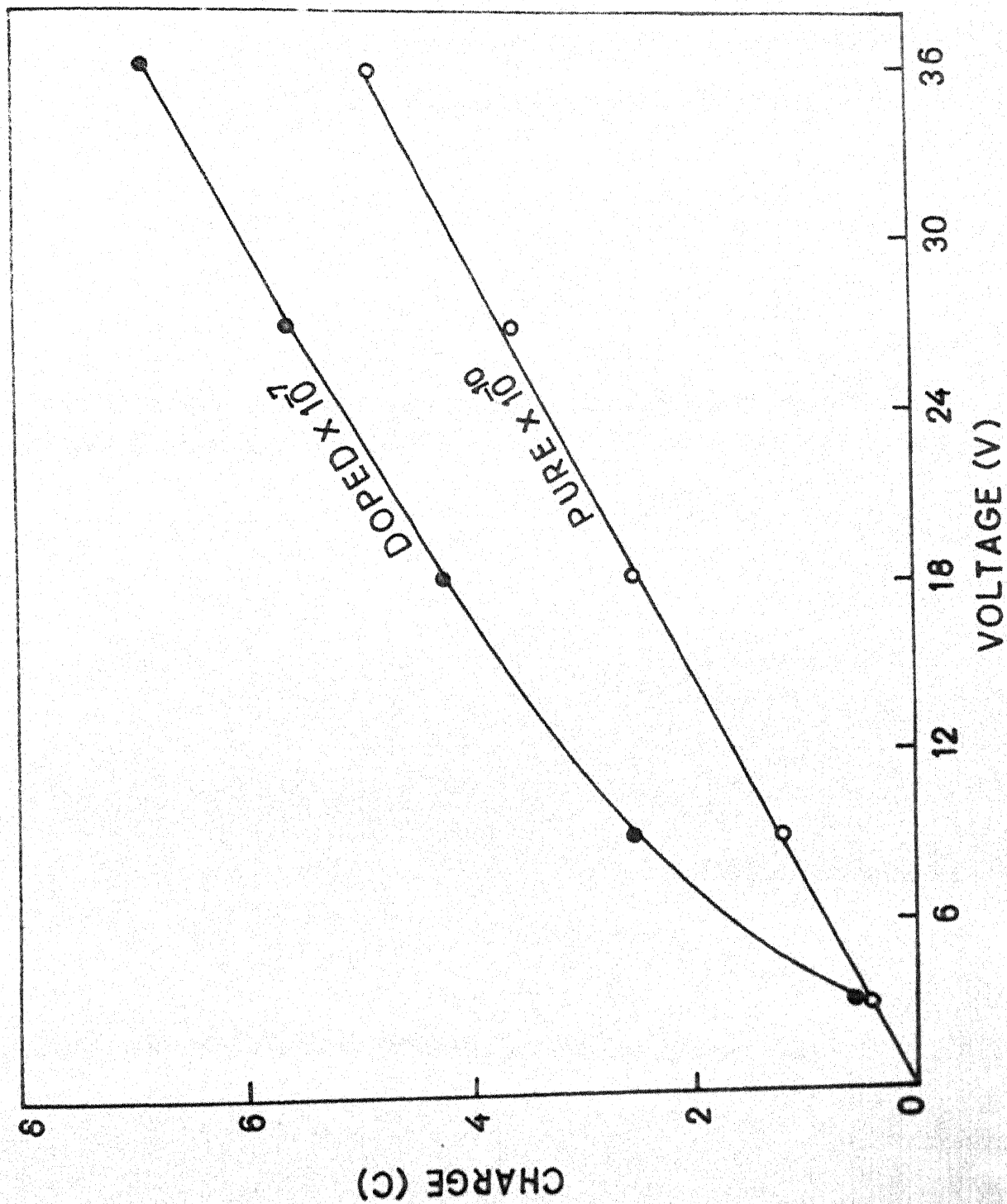


FIG. 5.3-CHARGE RELEASED VS. POLARIZING VOLTAGE.

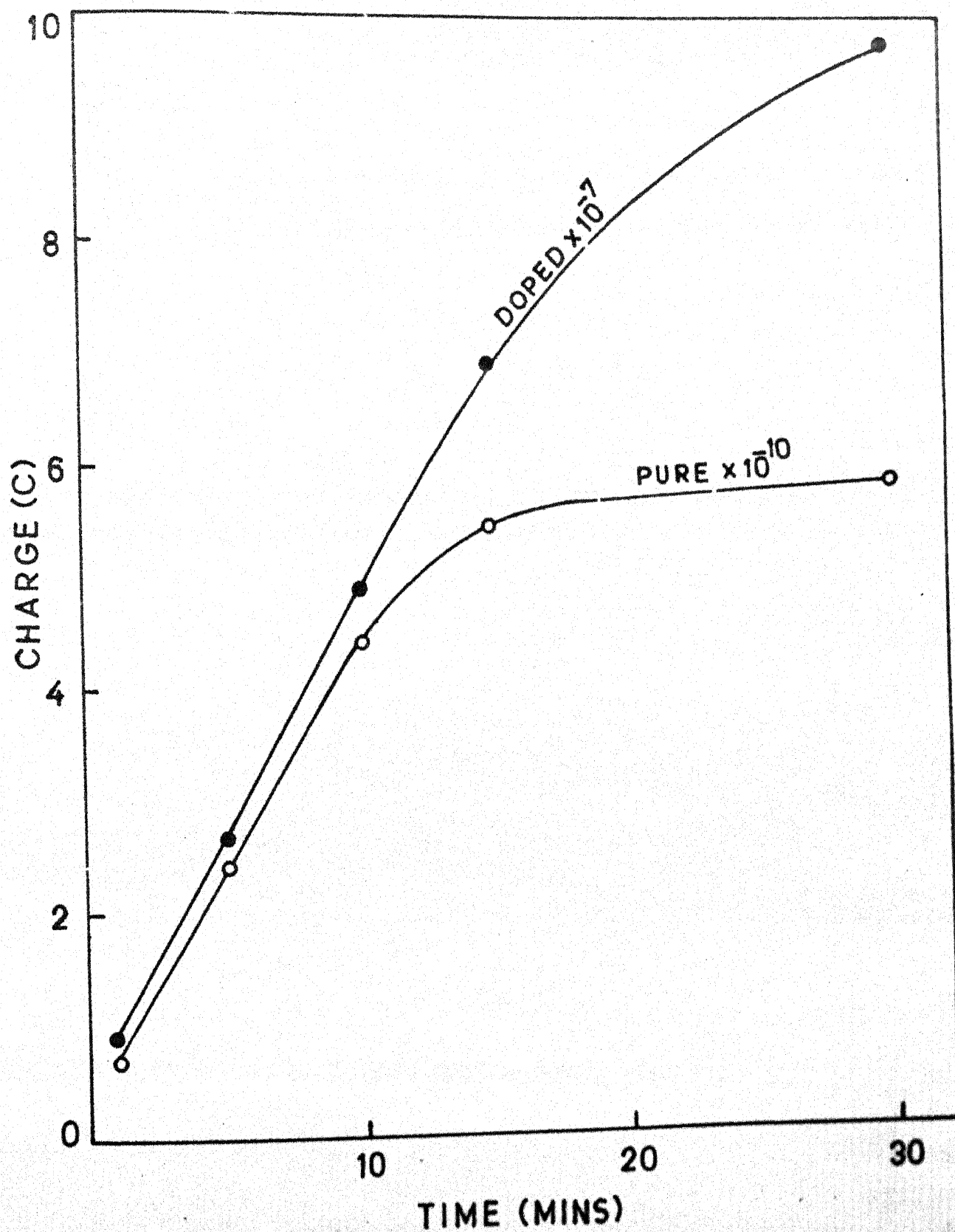


Fig. 5.4—CHARGE RELEASED VS. POLARIZING TIME.

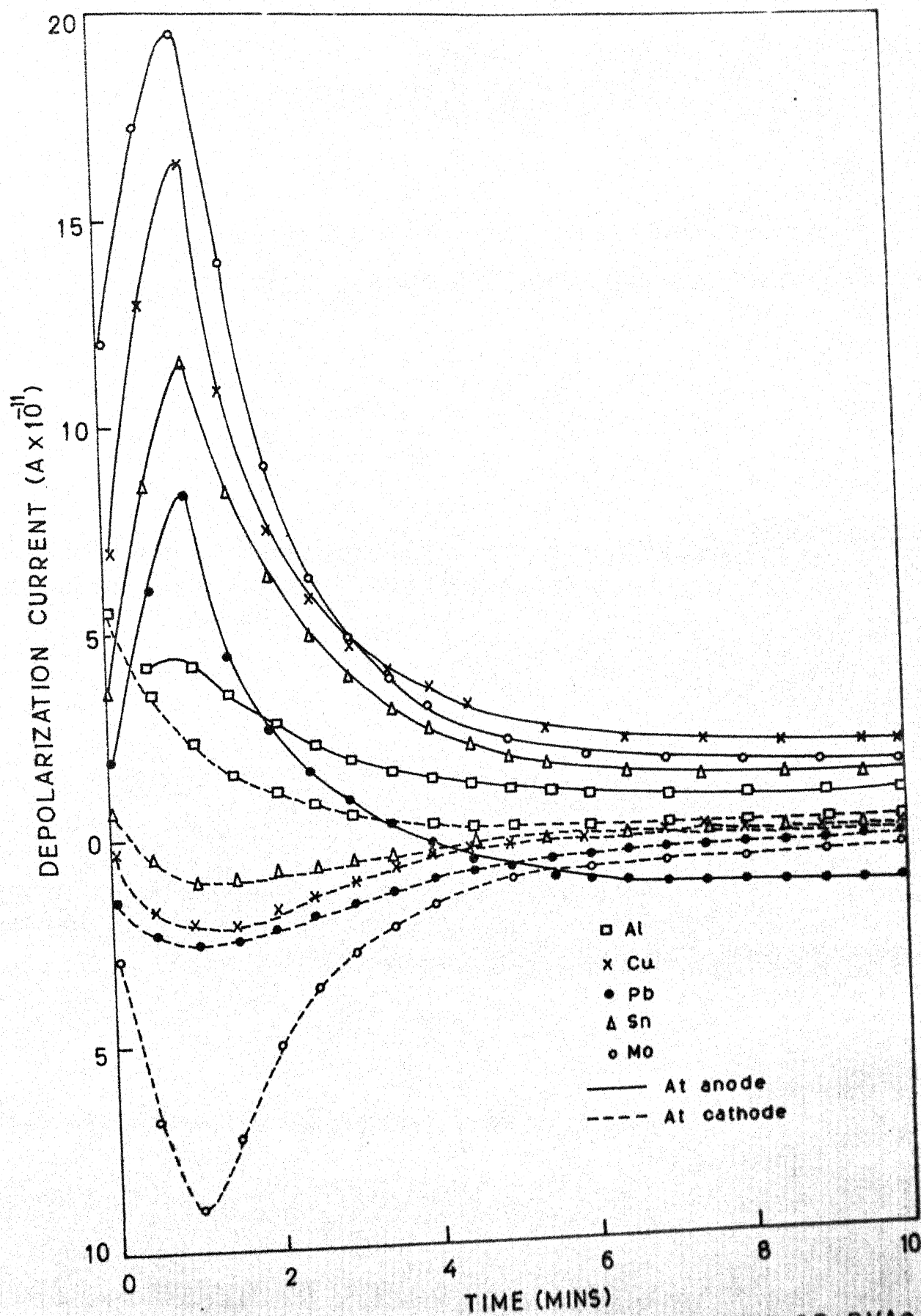


Fig. 5.5—DEPOLARIZATION CURRENT DECAY MODE OF PVAc FILMS ON VARIOUS METALS.

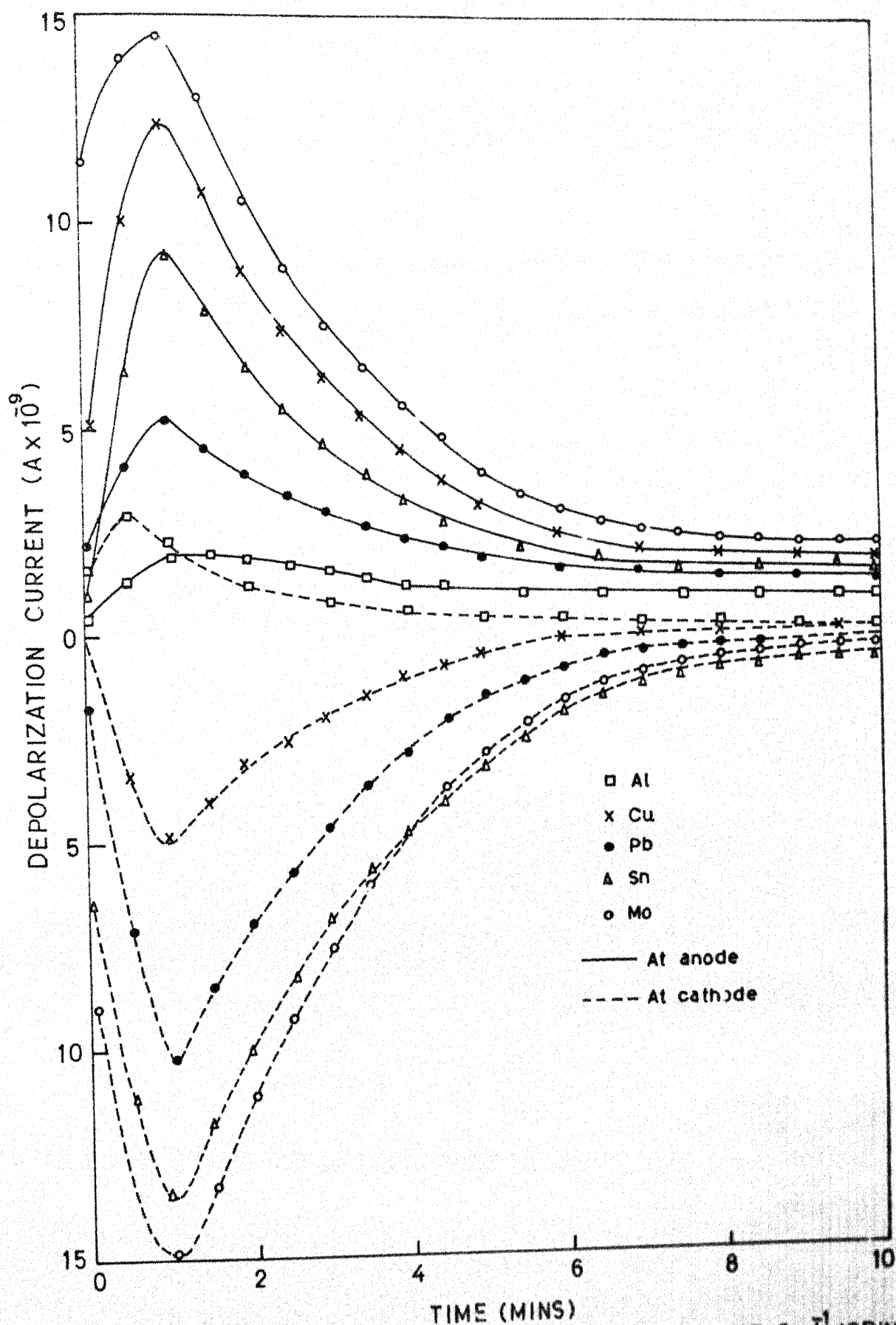


Fig. 5.6—DEPOLARIZATION CURRENT DECAY MODE OF 5 g l^{-1} IODINE DOPED PVAc FILMS ON VARIOUS METALS.

was calculated by integrating the current versus time curve. The charge versus polarising voltage has been plotted in fig 5.3 for pure and iodine doped films. Released charge increases linearly with voltage upto about 36 V beyond which the increase in charge with voltage becomes less than that expected according to linear relationship. Approximately thousand times more charge is released when PVAc is doped with iodine. The variation in charge with polarising time has been shown in fig 5.4 for both the samples. The charge versus time plot is linear upto about 10 mins beyond which a strong saturation effect is seen.

Electrode effect on photodepolarisation current was studied by growing the pure and doped films on Al, Pb, Cu, Sn and Mo substrates. These metals were chosen in order to provide a range of work function. Photoelectrets were formed in 5 mins by 9 V. Fig 5.5 shows the decay modes of photodepolarisation current for pure PVAc at both the electrodes while fig 5.6 illustrates the effect of electrode material on photodepolarisation current from doped films. Currents at both the electrodes for two types of films depend considerably on electrode forming material. The initial maximum value and final steady value of current is changed drastically with the choice of electrode system. The currents released at the anode are much larger than those released at the cathode for PVAc. Due to doping the current is enhanced by two orders of magnitude and the asymmetry at the two electrodes is diminished. The ratio of the currents released at the two electrodes changes with the change of

electrode material. The charge released calculated by integrating the current versus time curve is listed in table 5.1.

Table 5.1

Charge released at the two electrodes for
Different metal contacts.

Electrode material	Charge in C x 10 ⁻⁸			
	PVAc Electret		Iodine doped PVAc electrets	
	Anode	Cathode	Anode	Cathode
Al	1.05	0.42	75	42
Cu	2.07	0.30	210	252
Pb	1.17	0.75	147	171
Sn	2.79	0.48	285	75
Mo	3.15	1.50	360	303

More charge is released at the anode than at the cathode by PVAc electrets. Doping tends to equalise the charges released at the electrodes.

5.3 Discussion

When the absorption spectra and photo-conductivity spectra for the majority of polymers are compared, a direct correspondence between them can be found. At the same time, by analogy with low molecular weight organic semi-conductors, it

may be assumed that light causes singlet-singlet transitions²⁵². The absorption of a photon in a polymer leads to the formation of an exciton which can migrate freely within the limits of a region of conjugated bonds. Cherkasov et al²⁵³ in an interpretation of the absorption and diffuse reflection spectra of polystyrene have indicated the possibility of formation of free carriers by dissociation of excitons generated by optical excitation. Preliminary irradiation of the polymers with UV light greatly increases their photoconductivity and it may be argued that UV light can ionise conjugated molecules, liberating photoelectrons, which are retained in the structure of the polymer and creating positively charged local centres which can serve as electron traps. On long wave irradiation, excitons are produced which are destroyed on defects (including defects created by UV radiation) with the formation of a trapped electron and a mobile hole.

When a photo-conducting material is illuminated with radiation, electrons and holes are produced. If a d.c. voltage is simultaneously applied across the sample, these holes and electrons move to negative and positive terminals respectively. At any given temperature a number of defects are usually present in a material. So there will be a number of trap levels present in the energy gap due to the interactions of these impurities with the ions of the sample. These defects can capture a hole or an electron. Thus the carriers generated by the photons can be trapped in certain levels in the material. These trapped holes

and electrons give positive and negative charges on either side of the sample.

The total current produced while reilluminating the sample can be due to two effects²⁵⁴:

- (a) Current due to the motion of carriers generated by photons and
- (b) Current due to dark polarisation.

The former (a) is given by

$$J = J_p + J_n$$

where $J_p = p \cdot e \cdot \mu_p \cdot E$ and $J_n = n \cdot e \cdot \mu_n \cdot E$

where n and p are number of electrons and holes created by photon irradiation, μ_n and μ_p are mobility of electrons in conduction band and holes in valence band. E is the electric field.

So this current depends mainly on the number of carriers ejected out of their traps due to reillumination of the sample. The later (b) includes the current produced by :

- (1) The motion of ions which have been displaced during polarisation.
- (2) The decay of stripping charges produced by the close contact of the metallic electrode and the dielectric.
- (3) The decay of the sprayed ions from the electrode on

the surface during polarisation especially at high fields, and

- (4) The thermal current which depends on the temperature of the sample.

During the depolarisation two main processes are taking place :

- (1) The ionic charges and stripping charges produced due to dark polarisation decay by recombination and lattice relaxation processes. This decay is very slow.
- (2) A number of electrons and holes trapped near the conduction and valence bands first get sufficient energy to come out to the conduction and valence bands respectively to contribute to the flow of current. As time goes on the current decays gradually which means that the number of free carriers decreases. At this time the current contribution comes mainly from carriers which are trapped well inside the energy gap and require sufficient energy to get themselves into the conduction and valence bands.

It has been possible to observe the spectral sensitization of the photo effect in polymers, in particular polymers with triple bonds and polyacetylenes. Two explanations exist for the sensitization of polymers due to doping²⁵⁵. One connects

this effect with the transfer of excitation energy from the adsorbed molecules of the dopant to the carriers trapped in the local levels, and their excitation into the conducting state. According to the other model, the process of sensitization consists in the transfer of an electron from the dopant to the semi-conductor. Since some of the dopants do not possess photoelectric sensitivity, the first mechanism is preferable. Because sensitized photo-conduction is carried out by holes, the transfer of excitation energy to the polymer apparently leads to the ejection of an electron from a completely filled band into local levels with the liberation of holes taking part in photo-conduction or (which is the same thing) to the excitation of holes into the valence band from the trapping levels.

The observed change in the intrinsic photoelectric sensitivity of a polymer in the presence of a dopant is not yet completely clear and is possibly connected with the nature of the traps created by the adsorbed molecules of the dopant. The increase in the photo-conduction of the polymer on the addition of traces of iodine may be regarded as a peculiar sensitization phenomenon. In this case the influence of the iodine may be exerted by the second mechanism.

5.3 (a) Current Decay Mode

Depolarization current decay modes of pure and iodine doped photoelectrets (fig 5.1 and 5.2) consists of two parts. Initially the current decays rapidly and then slowly.

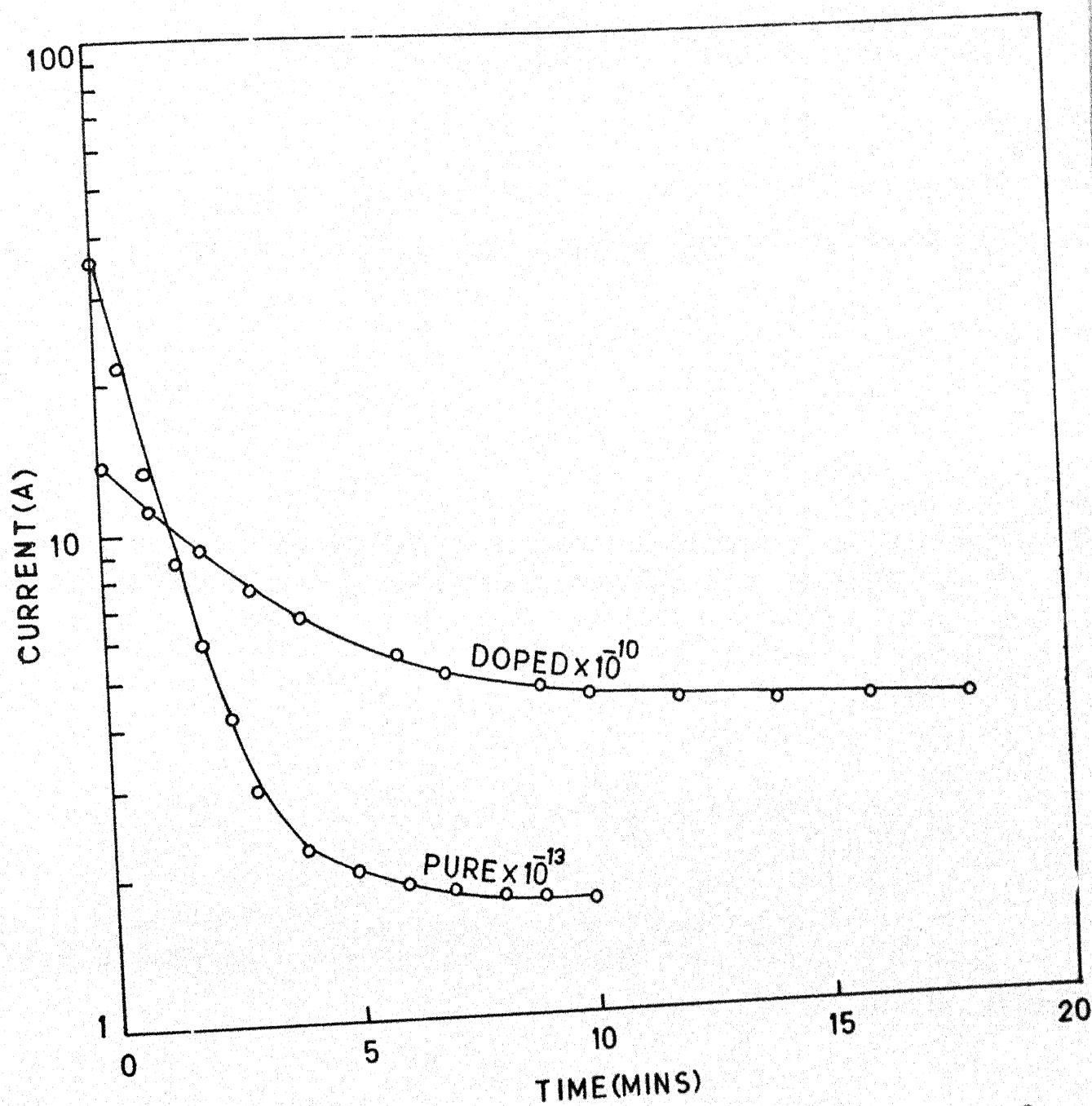


Fig. 5.7—SEMILOG PLOT OF CURRENT VS. TIME OF CURVES C OF Fig. 5.1.

The rapid decay of current is associated with the holes while in the slow decay region, current is mainly contributed by the electrons²⁵⁶. The holes are trapped weakly close to the boundary levels and the electrons display a spread in the bulk. The decay curves C of fig 1 and of its insert have been replotted on a semilogarithmic scale in fig 5.7 (others were also replotted and were found to be approximately parallel). The exponential decay of current $i(t)$ can be described by²⁵⁷ :

$$i = i_0 \exp \left(- \frac{t}{\tau} \right) \quad \dots (5.1)$$

where i_0 is the initial current and τ is the relaxation time which is represented by :

$$\frac{1}{\tau} = \gamma_0 \exp \left(- \frac{E}{kT} \right) \quad \dots (5.2)$$

where γ_0 is the frequency of escape from the trap, E the activation energy for the traps, k Boltzmann constant and T the absolute temperature. The slope of the plot of fig 5.7 yields the value of τ and taking $\gamma_0 = 10^{12}$, trap depth is calculated. These values are listed in table 5.2.

Table 5.2

	Fast decay region		Slow decay region	
	Relaxation time (S)	Trap depth (eV)	Relaxation time (S)	Trap depth (eV)
Pure PVAc	72	0.82	3139	0.92
Doped PVAc	307	0.86	2159	0.91

Relaxation time and trap depth for pure and doped PVAc in fast and slow decay regions of current.

No appreciable energy differences are found between shallow and deep traps in the two types of films. However, it may be said that doping of the matrix with iodine has an effect of increasing the trap depth. This fact can not be explained if it is assumed that mobile charges are produced as a primary process of light absorption but is easily understandable in terms of creation of free charges via exciton formation²⁵⁸ where doping reduces the relaxation time.

5.3 (b) Build-up of Polarization with Field

Released charge versus polarizing voltage for PVAc (fig 5.3) is characterised by a straight line passing through the origin. This shows that there is a voltage dependant source of electrons. This may be in the bulk or at the negative electrode. Doping enables the polymer to store thousand time more charge which saturates with the applied field (fig 5.3). This supports the trap filling hypothesis²⁵⁹. At high fields the increase in polarization is slowed down because of the saturation of the number of traps available for polarization. When all the traps are filled, any excess holes and electrons will recombine rapidly. Iodine forms CT complexes with PVAc and creates new trapping sites²⁶⁰ in the matrix exhibiting enhanced polarizability.

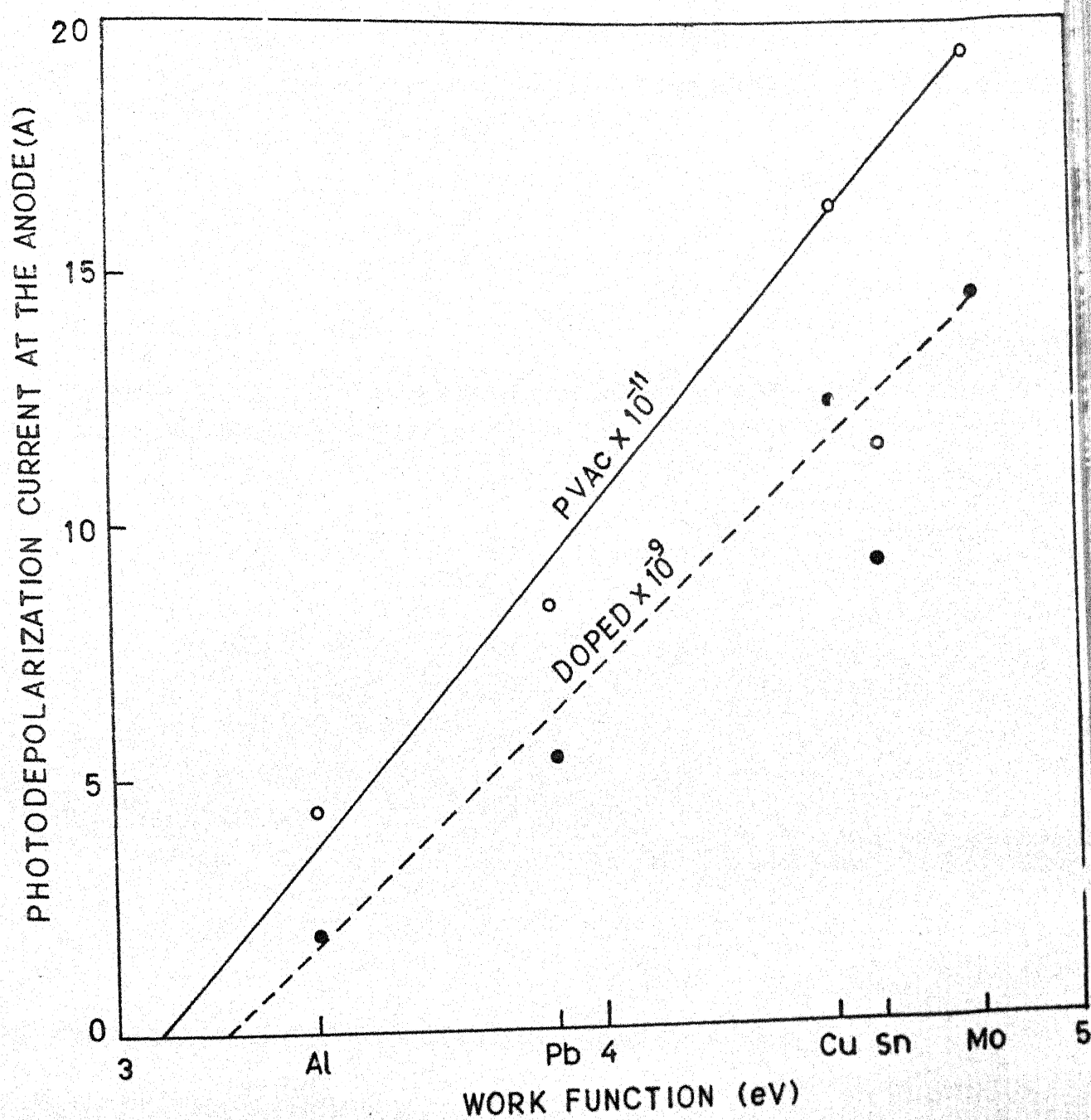


Fig.5.8—PHOTODEPOLARIZATION CURRENT AT ANODE VS. METAL WORK FUNCTION.

5.3 (c) Polarization versus Time

The field effect on polarization is understandable when the dependence of polarization on time is taken into account. Charge released as a function of electret forming time has been shown in fig 5.4 for two types of films. The build up of polarization (P) with time for pure and doped PVAc are seen to have the form²⁴ :

$$P = P_{\max} \left[1 - \exp \left(-\frac{t}{\tau} \right) \right] \quad \dots (5.3)$$

The slowing down of the rate of increase of polarization results from the fact that as the polarization builds up, the effective field on mobile charges decreases.

5.3 (d) Electrode Effect

Considerable electrode effect on photo-depolarization current in pure and iodine doped PVAc films (fig 5.5 and 5.6) has been observed. The asymmetry between the current and the charge released at the electrodes indicates the majority of holes²⁶. Incorporation of iodine in the polymer creates a high density of trapping centres²⁶⁰ and so the doped films store more charge. The presence of impurities in the polymer reduces the life time of the excitons increasing the probability of formation of mobile charges via excitons. In fig 5.8 the initial maximum value of depolarization currents at the anode have been plotted against metal work function for pure and doped PVAc. The plots

are straight lines for both the samples, showing that the amount of charge carriers, supplied by the metal and injected into the sample increases with decreasing metal work function²⁶¹. The present results of electrode effect on photo-depolarization current can be qualitatively understood in terms of a dielectric loss model²⁶² based on the tunneling of electrons from the metal into traps located within the polymer near the interface.

5.4 Conclusions

Photo-depolarization current studies of pure and iodine doped PVAc films enable one to draw the following conclusions :

- (1) Decay of depolarization current occurs in two parts. The rapid decay is due to detrapping of holes while the slow one is due to untrapping of electrons.
- (2) Iodine forms CT complexes with PVAc and creates new trapping sites in the matrix enhancing the depolarization current and the released charge.
- (3) Linearity of released charge versus field for PVAc indicates charge injection mechanism.
- (4) Polarization in pure and doped films saturates with time.
- (5) Electrode effect on depolarization current indicates that the charge injection from electrode into the polymer increases with decreasing metal work function.

CHAPTER VI

Am Adhar Shiv Adhar Stores

DIELECTRIC PROPERTIES

6.1 Introduction

The dielectric behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their application in capacitors for micro-electronics. To obtain high values of capacitance, the dielectric constant should be high and the thickness be small. Due to the difficulty of obtaining structurally continuous and stable ultrathin films, capacitor applications are generally limited to thick films.

The evaluation of dielectric properties of insulator films²⁶³⁻²⁶⁷ is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperatures. As all the other electrical parameters of dielectrics, the permittivity depends on the changable external factors such as the frequency of voltage application, temperature, pressure, humidity etc. In a number of cases these dependences are of great practical importance.

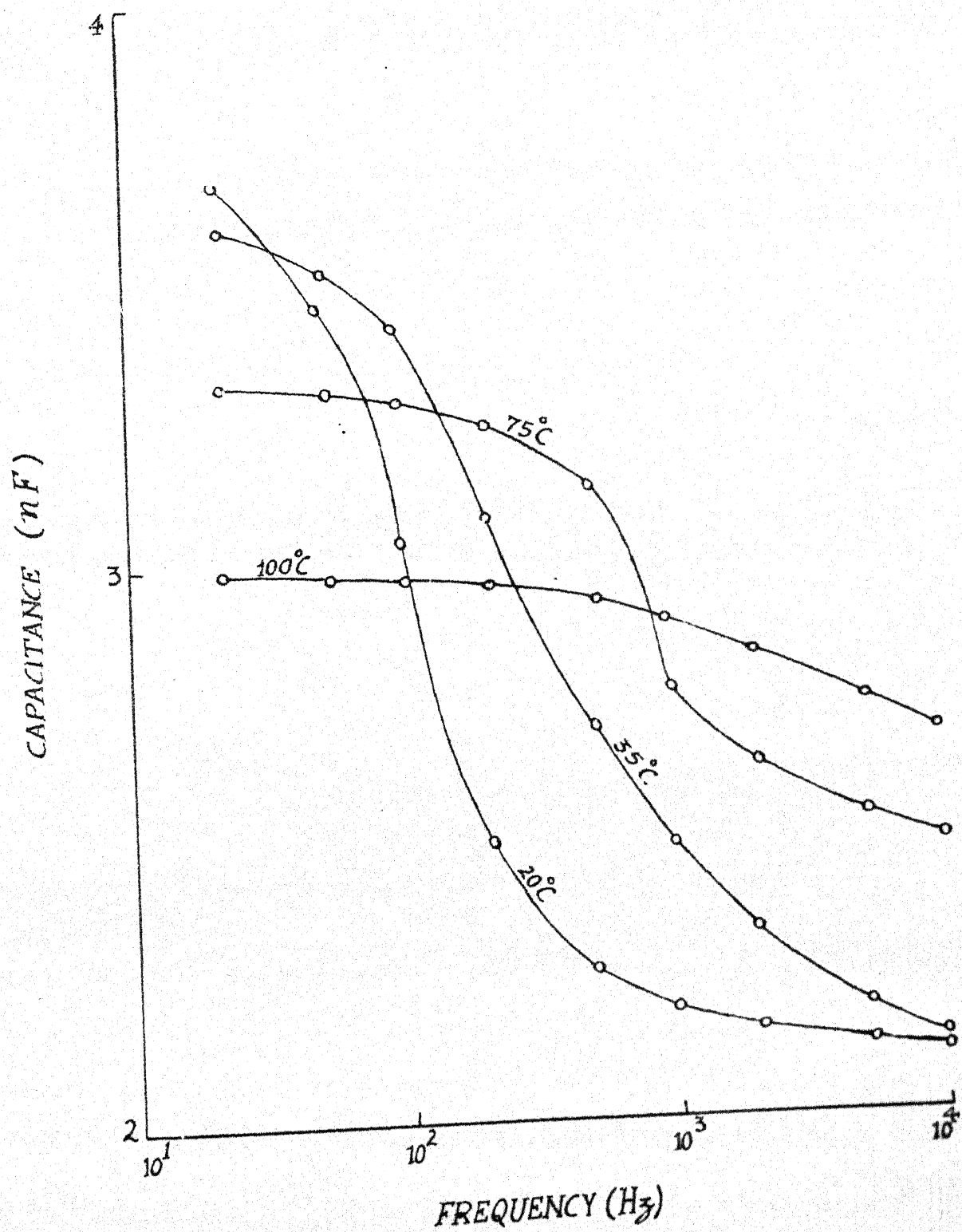
Recently dielectric properties of several polymers²⁶⁸⁻²⁷⁴, polar and nonpolar have been investigated. Some general relations between dielectric properties have been discussed, distinguishing between resonance phenomena that commonly occur in the optical region and relaxation phenomena which occur in polymers at the lower frequency regions. It has been shown how the real and imaginary parts of the complex

dielectric constant are related. In nonpolar polymers, the dielectric constant depends primarily on the density, but little is known regarding the nature of the dielectric loss. Attention has also been paid to polar polymers. After some preliminary remarks on the nature of dielectric dispersions, some phenomenological notions of dielectric dispersions have been considered. Attempts have been made to relate theory and practice. The topics, such as phase transitions, anisotropy and in homogeneity, have been dealt with.

Dielectric relaxations in polyvinylidene fluoride were studied by Sasabe et al²⁷⁰. They observed three distinct absorption peaks (α_c , α_a and β) in the frequency range from 0.1 to 300 Hz in the temperature range -66 to 100°C. The α_c absorption is related to molecular motion in the crystalline region. The α_a absorption can be interpreted as due to the micro-Brownian motion of the amorphous main chains. The β absorption is attributed to local oscillations of the frozen main chains. Kakutani and Asahina²⁷¹ studied low temperature absorptions of polyvinyl chloride and concluded that the β_1 and β_2 processes are the results of molecular motion in crystalline and amorphous regions of the polymer respectively. Low temperature dielectric relaxation in polyethylene and related hydrocarbon polymers was investigated by Philips²⁷⁵. He uses a simple quantum mechanical model of relaxation process to explain the experimental results. According to this process, a particle in a double potential well tunnels from one well to the other with emission or absorption

of a phonon. It is deduced that the particle is a proton and the loss peak is ascribed tentatively to hydroxyl rotation in the crystalline regions of the polymer. Results of Kawamura et al²⁶⁸ on dielectric properties of copolymer of methyl-methacrylate with n-butyl methacrylate lead to the following conclusions : (1) The loss peak temperature attributed to side chain relaxation (β) varies with the comonomer ratio when the comonomer does not have an α -methyl group but remains almost unchanged for comonomers having an α -methyl group. (2) In both cases, the β -peak height decreases with increasing ratio of comonomer. It is suggested on the basis of the above facts that the moving unit in the side chain relaxation consists of a single side chain with a segment of the backbone chain and that the change in mobility of the side chain upon copolymerization results from the distortion of the helical structure of the backbone chain due to random distribution of α -methyl groups.

Though there is a wide literature available on dielectric properties of polymers, yet a few reports²⁷⁶⁻²⁷⁸ exist on impurity doped polymers. Kokasi and Ieda²⁷⁶ have doped high and low density polyethylene. One of them has the loss maximum dependent on the amount of the impurity and is related to the relaxation of a dipole orientation of the impurity. Another shows an odd behaviour named retrogressing phenomenon near the melting point of polyethylene and can not be detected in the amorphous polystyrene doped with the same impurity. An interfacial polarization is proposed assuming a model which is



CAPACITANCE VERSUS FREQUENCY AT DIFFERENT TEMPERATURES FOR PVAc

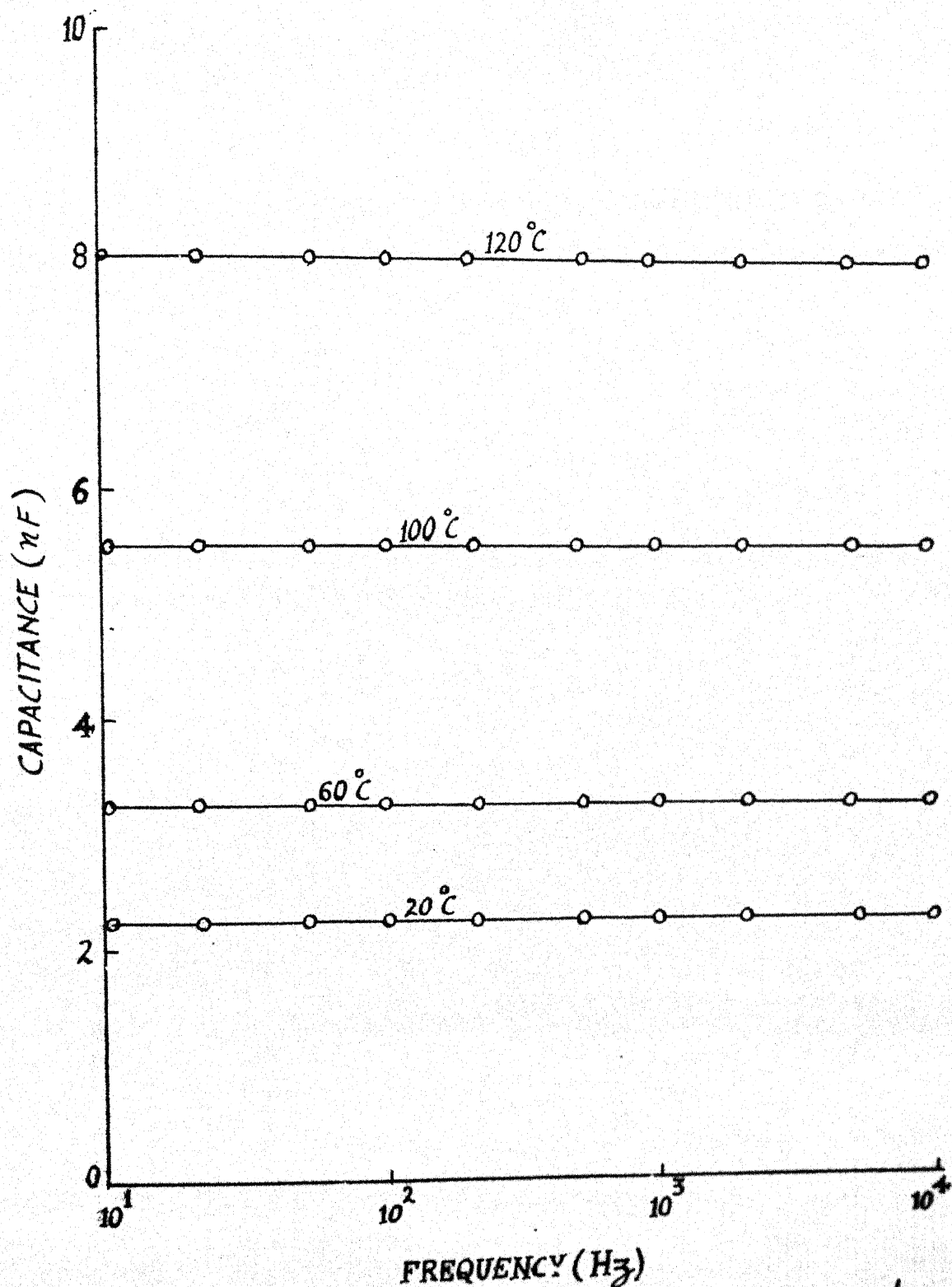
Fig-6.1

justified semi-quantitatively. The retrogressing phenomenon is explained by the change of the layer thickness that affects the dielectric relaxation time of the model. Kulshretha and Srivastava²⁷⁷ doped polystyrene with chloranil and Shrivastava et al²⁷⁸ with copperphthalocyanine and observed interfacial polarization in the measurement of dielectric losses of the polymer.

Less has been reported on dielectric properties of PVAc²⁷⁹ and it seems to carry out further investigations to understand the dielectric behaviour of the polymer. This chapter reports on capacitance and dielectric loss factor of pure and iodine doped PVAc films as a function of temperature and frequency in audio frequency range.

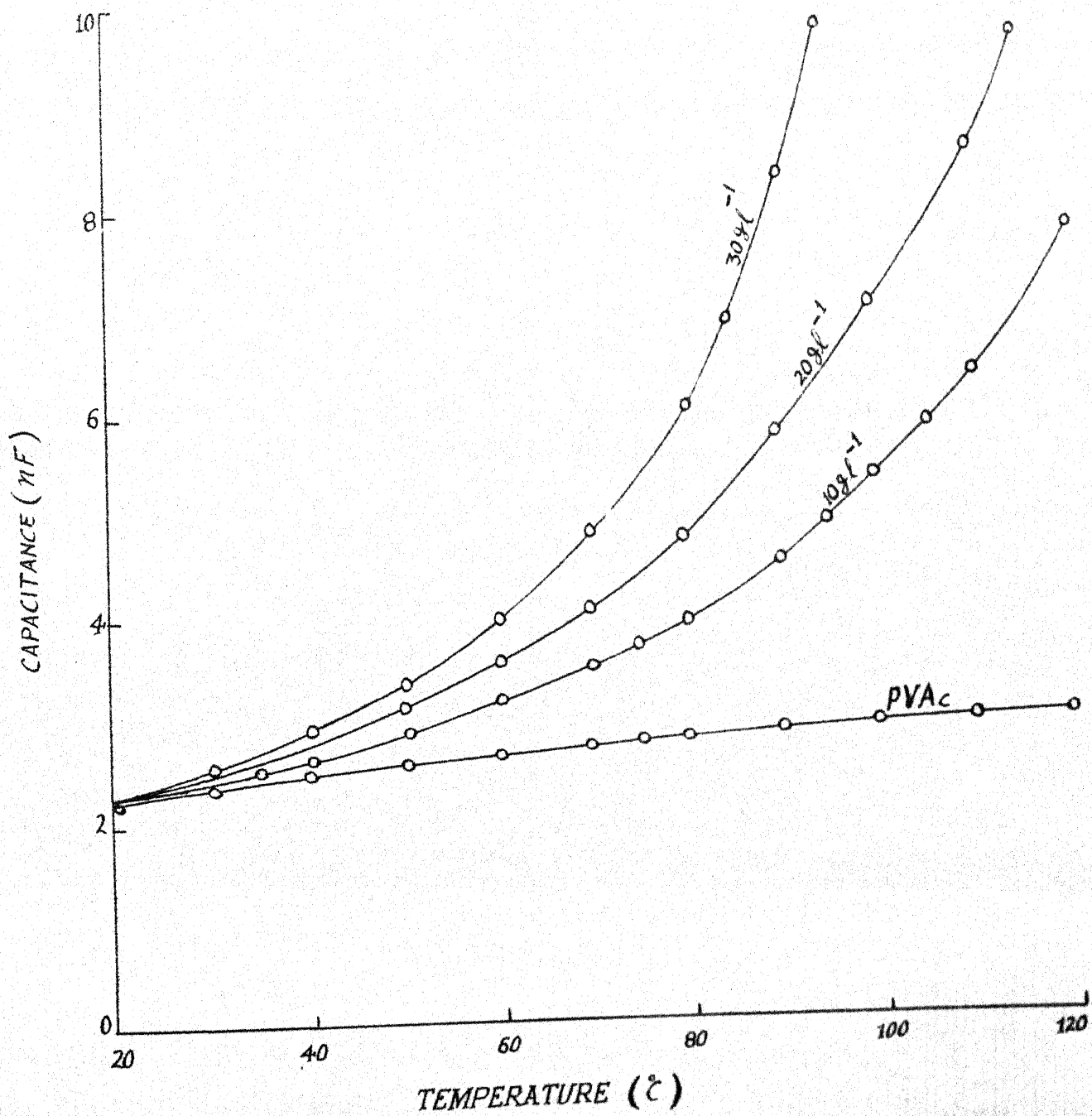
6.2 Results

Dielectric properties of polymers are investigated by measuring simultaneously the capacitance and the losses at regularly varying temperature and frequency. Capacitances as a function of frequency for PVAc film at temperatures 20, 35, 75 and 100°C are shown in fig 6.1. At all the temperatures for lowest frequency of measurement, the capacitance is maximum and decreases with increasing frequency and assumes a certain minimum value at the highest frequency. The rate of fall of capacitance with frequency is largest at the lowest temperature. As the temperature is increased, this rate is decreased. To study the variation of capacitance with frequency for iodine



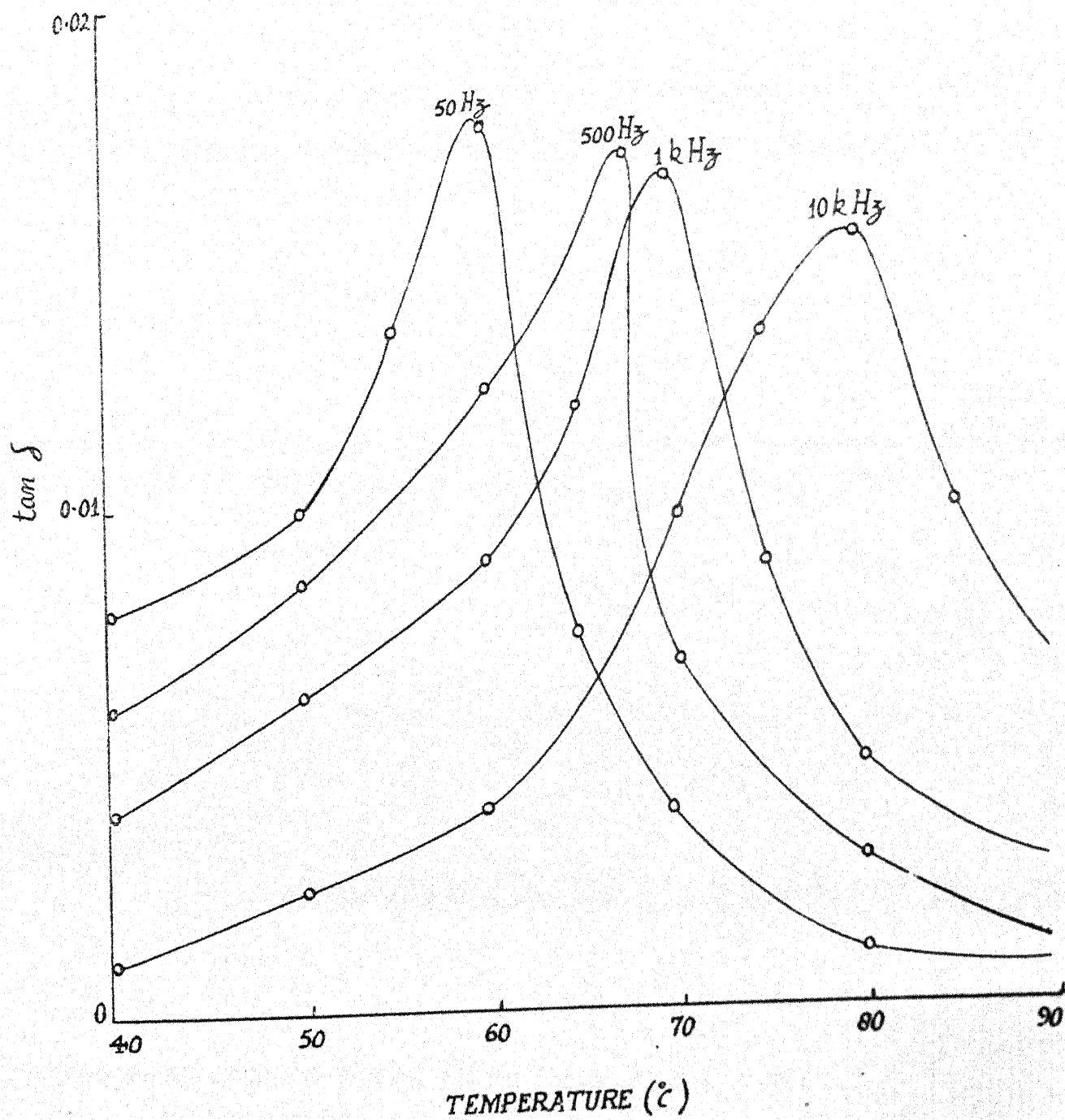
CAPACITANCE VERSUS FREQUENCY AT DIFFERENT TEMPERATURES FOR 10g l^{-1} IODINE DOPED PVAc

Fig-6.2



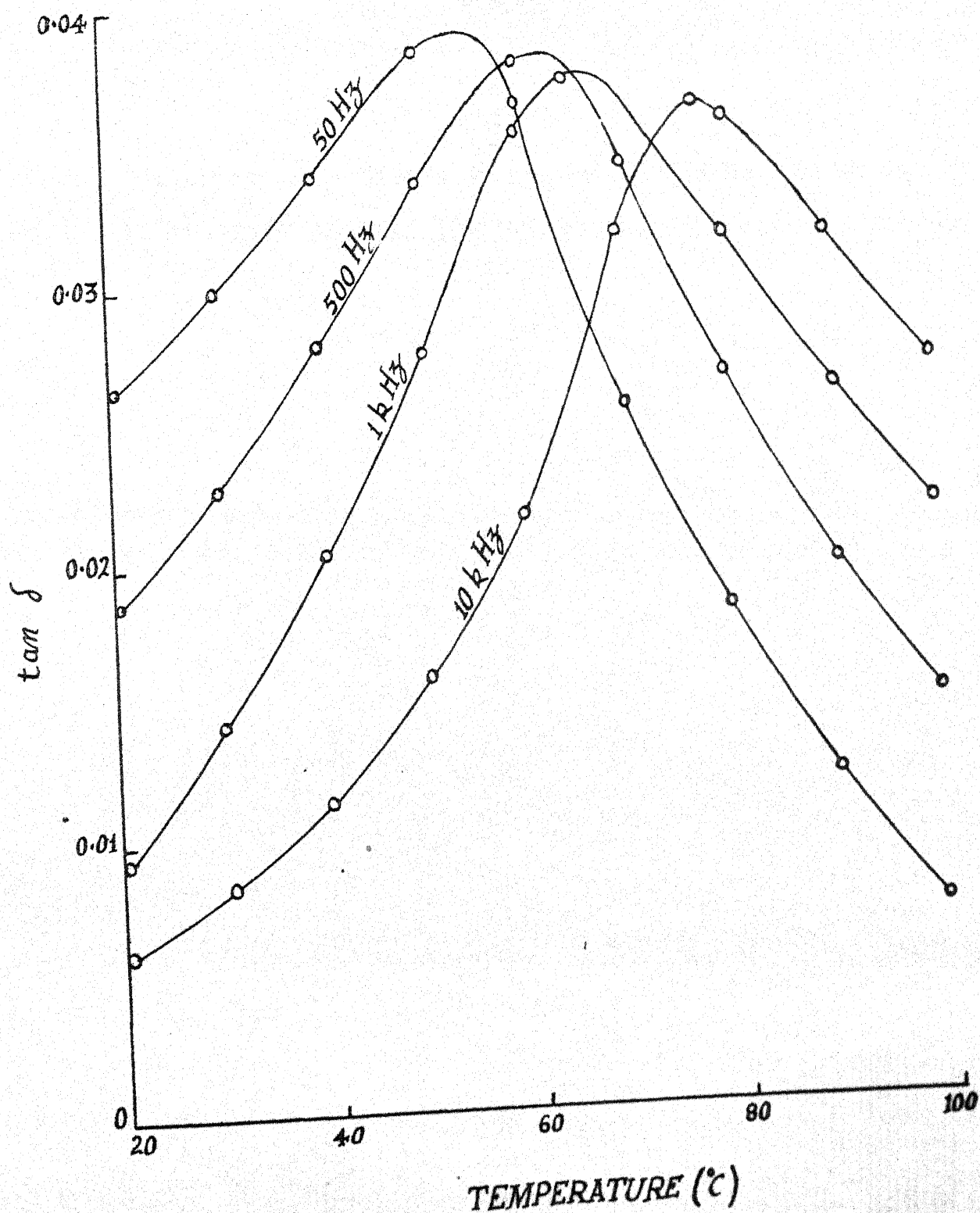
CAPACITANCE VERSUS TEMPERATURE FOR PURE AND IODINE DOPED PVA_c AT 1 kHz

Fig-6.3



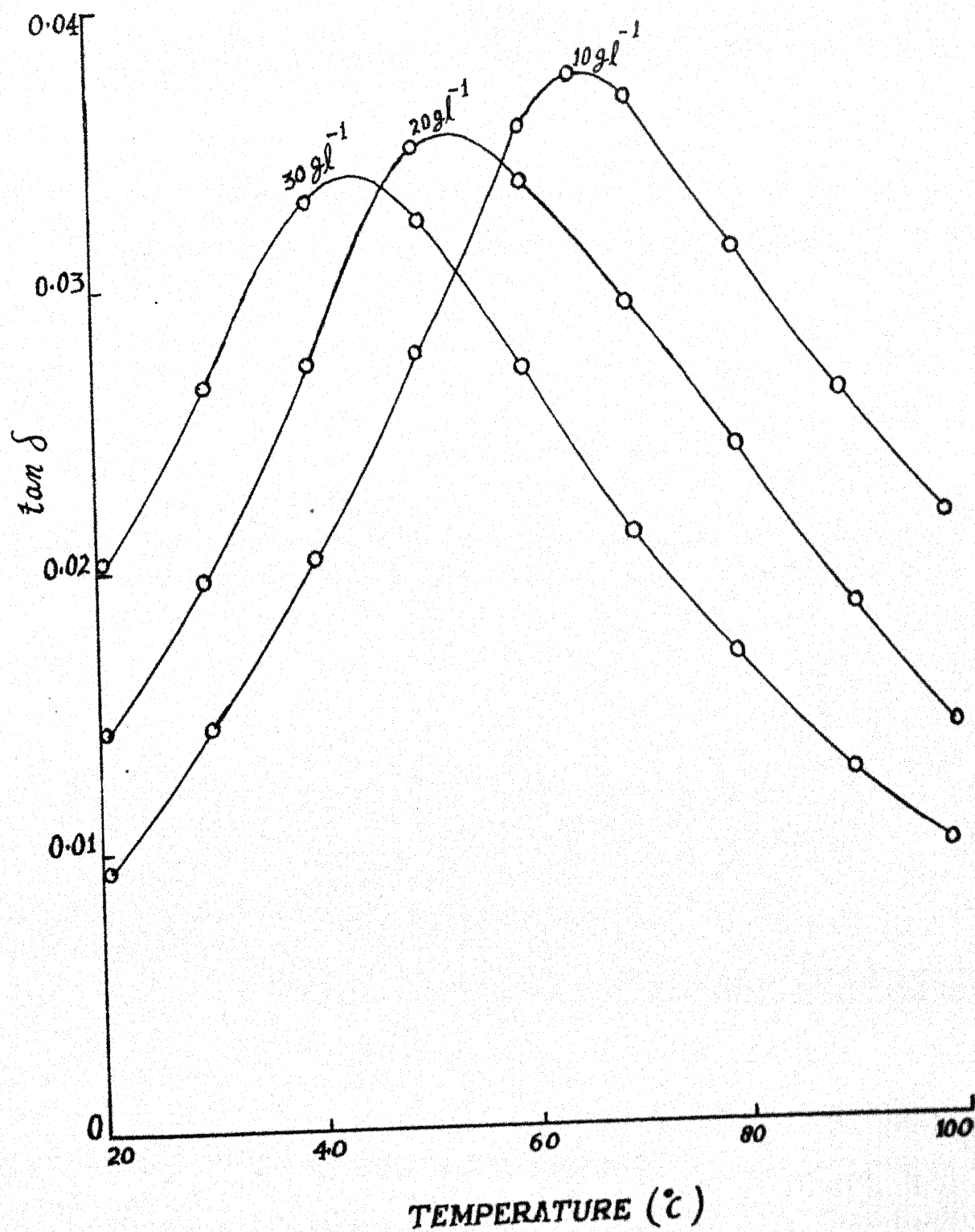
LOSS TANGENT VERSUS TEMPERATURE FOR PVA_c AT VARIOUS FREQUENCIES

Fig 6.4



LOSS TANGENT VERSUS TEMPERATURE FOR 10g l^{-1} IODINE DOPED PVAc AT VARIOUS FREQUENCIES

Fig-6.5



EFFECT OF IODINE CONCENTRATION ON TEMPERATURE VARIATION OF LOSS TANGENT AT 1 kHz

Fig 6.6

doped PVAc, the films doped at 10 g l^{-1} concentration were employed. The capacitance versus frequency at 20, 60, 100 and 120°C is shown in fig 6.2. There is no change in capacitance with frequency. The films incorporating iodine in higher concentrations also exhibited similar results, fig 6.3 shows the temperature dependence of capacitance for pure and 10, 20 and 30 g l^{-1} iodine doped PVAc films in the temperature range $20 - 120^{\circ}\text{C}$ at 1 kHz. The capacitance of all types of films increases with the increase in temperature. The increase in capacitance with temperature is least for pure PVAc film. Due to doping of the matrix, capacitance of the film is not changed at 20°C , but as the temperature increases the capacitance is increased. This increase in capacitance with temperature is enhanced when the concentration of iodine is increased.

Fig 6.4 exhibits the variation of $\tan \delta$ (loss tangent) with temperature at different frequencies for PVAc film while fig 6.5 that for 10 g l^{-1} iodine doped film. For PVAc a loss maxima at 80°C is observed at a frequency of 10 kHz which shifts to lower temperature as the frequency is decreased. Doped film exhibits comparatively larger losses at all the temperatures and frequencies. The loss maxima for the doped film is observed at 78°C at a frequency of 10 kHz which also shifts to lower temperature with the decrease in frequency. Therefore, doping of PVAc with iodine enhances dielectric loss and shifts loss maxima to a lower temperature. Fig 6.6 shows the effect of iodine concentration on temperature variation of

loss tangent at 1 kHz. Due to increase in dopant concentration, the losses are decreased. The loss maxima is shifted to a lower temperature when more quantity of iodine is incorporated in PVAc.

6.3 Discussion

Permittivity is the basic parameter of a dielectric describing its properties from the view point of the process of its polarization or propagation of electromagnetic waves in it, or more generally from the point of view of the processes of its interaction with an electric field. Permittivity is a microscopic parameter of a dielectric which reflects the properties of a given substance in a sufficiently large volume but not the properties of the separate atoms and molecules in the substance. There are three well known types of polarization: electronic, ionic and dipole polarization.

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, to be more precise - the displacement under the action of an external field of the orbits in which negatively charged electrons move around a positively charged nucleus. This type of polarization occurs in all atoms or ions and can be observed in all dielectrics irrespective of whether other types of polarization are displaced in the dielectric. One specific feature of electronic polarization is the fact that when an external field is superposed, this type of polarization occurs during a very short

interval of time (of the order of 10^{-15}_S) i.e. the time of the period of oscillations of ultraviolet rays.

Ionic polarization is the mutual displacement of ions forming a heteropolar (ionic) molecule. A shorter time is required for the process of ionic polarization to set in, but it is longer than that for electronic polarization, i.e., $10^{-13} - 10^{-12}_S$. On the whole the processes of electronic and ionic polarization have much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of charges with respect to each other in the direction of the field. Apart from a very high velocity mentioned above with which the state of polarization sets in, it is important to bear in mind that the process of deformational polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required to polarize a molecule is completely returned to the energy source after voltage is removed. For this reason, deformational polarization does not entail any dielectric losses.

Polar dielectrics²⁸⁰⁻²⁸³ exhibit a tendency towards dipole or orientational polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye, to the rotation of the molecules of a polar dielectric having a constant dipole moment in the direction of a field. If orientational polarization is considered more strictly, it must be understood as the introduction

by an electric field of a certain orderliness in the position of polar molecules being in uninterrupted chaotic 'thermal' motion, and not as a direct rotation of polar molecules under the action of a field. For this reason, dipole polarization is connected by its nature with the thermal motion of molecules, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

After a dielectric is energized, the process establishing a dipole polarization requires a relatively long time as compared with that of practically almost inertialess phenomena of deformational polarization. More or less time is needed in any individual case. As distinct from deformational polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which transforms into heat in a dielectric i.e. this energy causes dielectric losses.

In polymers the dielectric loss behaviour may be attributed to the deformation of polymer chains²⁸⁴⁻²⁸⁶. The molecular flexibility of the chains are responsible for this characteristic property of the polymers. The other important mechanism for the dielectric losses in the polymers is considered to be the internal motions or the local movements of the molecular chains of the polymer. At high temperatures, especially at the glass transition temperature of the polymer such segmental motions are prominent. However, at low temperatures these motions become less significant.

6.3 (a) Frequency Dependence of Capacitance

The capacitance and hence the dielectric constant of PVAc decreases with the increase in frequency (fig 6.1). For the doped films, there is no change in capacitance with the change in frequency (fig 6.2). This is so because the polarisation settles itself during a very short period of time as compared with the time of voltage sign change. Dielectric constant of nonpolar polymers remains invariable with frequency. In case of polar polymers like PVAc, the dielectric constant begins to drop at a certain critical frequency and at very high frequencies it approaches the values typical of nonpolar polymers. In amorphous polymers, structural polarization (i.e. related to the loose structure of matter) is also possible. For this type of polarization, the capacitance falls with the increase in frequency²⁸⁷.

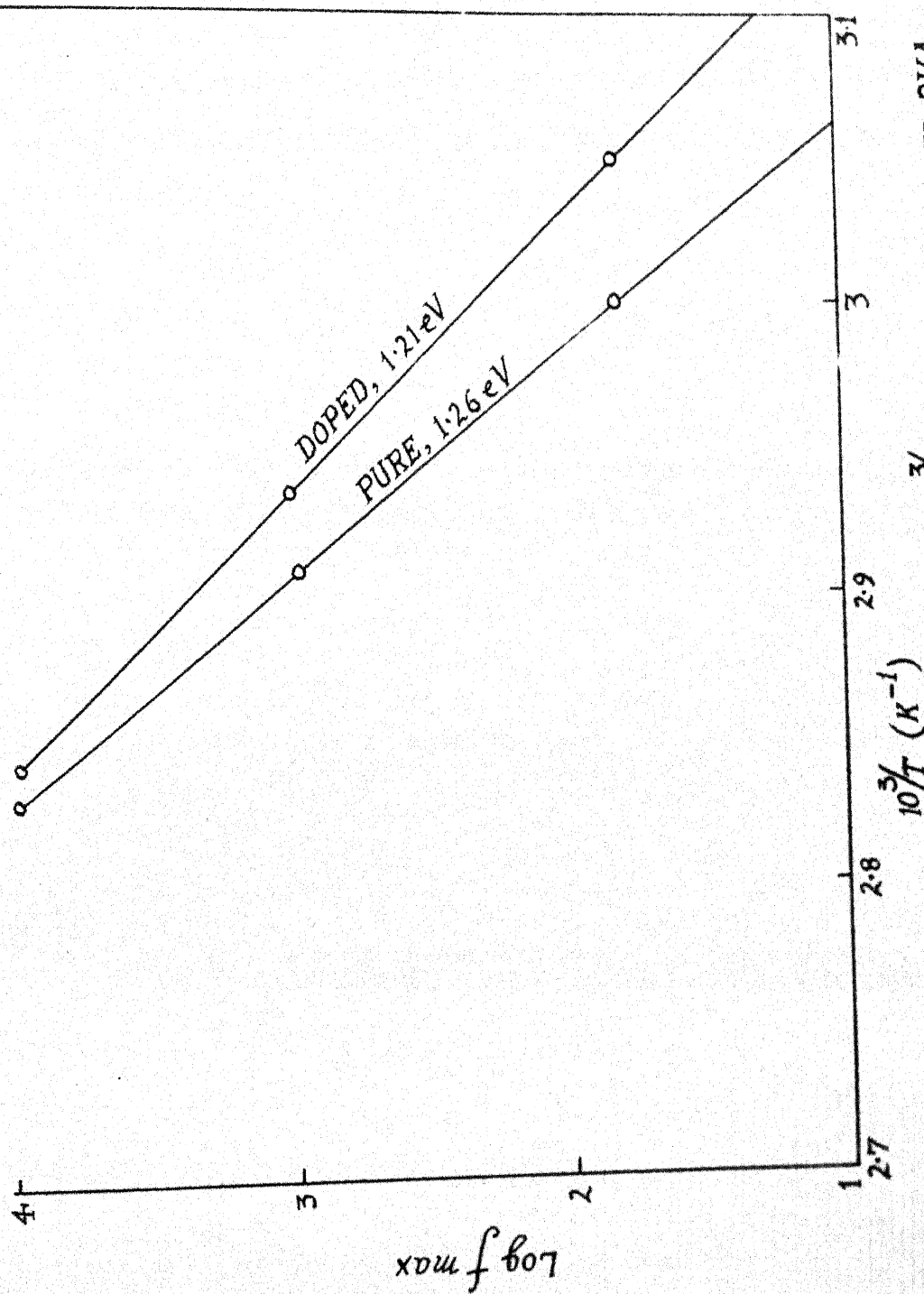
6.3 (b) Temperature Dependence of Capacitance

The increase in capacitance above the room temperature (fig 6.3) may be partly due to the expansion of the lattice and partly due to an ionic mechanism of polarization. The molecules can not orient themselves in polar dielectrics²⁸⁸ in the low temperature region. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. Addition of iodine forms CT complexes with the polymer and so the increase in capacitance with temperature is enhanced.

6.3 (c) Variation in Loss Tangent

Temperature transition corresponding to α -relaxation process has been observed above the glass transition temperature of PVAc (fig 6.4 and 6.5). The α -relaxation process in polymers is observed at temperatures above the glass transition of the polymer²⁸⁸. Though at the glass transition temperature the segmental motion is expected but at the temperatures above the glass transition temperature some thing larger than segments and possibly the entire molecular chain motion is expected. Polymers are considered to be the mixture of amorphous and crystalline regions. Above the glass transition temperature they seem to loose the intermolecular cohesive bondings and the association and dissociation processes involved are governed by thermodynamical equilibrium. Therefore, α -relaxation process in PVAc films may be attributed to the motion of the more mobile molecular chains in which the intermolecular forces between the crystalline regions are weakened due to thermally activated process. This weakening of forces causes the motion of the entire molecular chain and hence, the occurrence of α -relaxation.

Incorporation of iodine in PVAc softens the viscosity of the system and causes the α -relaxation to shift to the region of lower temperatures. The view is further supported by the observation that the increase in iodine concentration has an effect of displacing the loss maxima to a lower temperature (fig 6.6).



LOG OF MAXIMUM FREQUENCY VERSUS $10^3/T$ FOR PURE AND DOPED PVAc

Fig 6.7

Logarithm of frequency at which loss maxima occurs, has been plotted against inverse absolute temperature in fig 6.7 for pure and 10 g l^{-1} iodine doped PVAc film. The activation energy is calculated to be 1.26 eV for PVAc and 1.21 eV for iodine doped PVAc. Incorporation of iodine has an effect of reducing the activation energy. Besides molecular chain movements, the losses also occur due to electrical conduction which increase with the decrease of frequency²⁷⁸. This is also what has been observed presently. Mixing of iodine in PVAc increases the conductivity of the film and so the doped film exhibits more pronounced increase in losses with the decrease of frequency.

6.4 Conclusions

The present investigation on dielectric behaviour of pure and iodine doped PVAc films helps to conclude :

- (1) Dipole polarization involving ionic motion is prominent in PVAc. Doping of the matrix with iodine enhances the process of polarization.
- (2) The α -relaxation in the polymer is due to the motion of polymer chains. Addition of iodine reduces the viscosity of the system shifting α -relaxation peak to lower temperature.
- (3) Doping causes conduction losses.

- (4) Above the glass transition temperature of the polymer, main chains are mobilized and the mobilization is facilitated due to incorporation of iodine.

CHAPTER VII

Ram Adhar Shiv Adhar Stores

CO-RELATION OF DIFFERENT STUDIES

7.1 The present work was undertaken to understand the mechanisms taking place in electrical conduction and polarization of pure and iodine doped PVAc films. Since polarization and electrical conduction are caused by the motion in space of the electrically charged particles of a dielectric, there is a certain affinity between these two phenomena. It will be useful to find some typical differences between these phenomena.

During polarization the charges linked with the definite molecules of matter are brought into motion²⁸⁹. These charges can not leave the confines of a given molecule where as electrical conduction is caused by the motion (drift) of free charges (carriers) which can move in matter over comparatively large distances and in the limiting case, through the entire thickness of a dielectric from one electrode to the other²⁹⁰.

Polarization takes place in all the molecules of a dielectric - it is its bulk property. At the same time, conduction of a dielectric is often and practically fully determined by the presence of a slight amount of impurities²⁹¹ (contaminants) and is not attributed to its basic substance. Conduction of a dielectric can appreciably be weakened with purification of its substance. Therefore, when two or several dielectrics which do not interact chemically are mixed, the permittivity of the resultant mixture may be evaluated to a first approxi-

mation from the arithmetic rule of mixing. This rule may prove totally unsuitable for calculating the resistivity of a dielectric since even a slight addition of another substance may sometimes reduce by several orders the resistivity of the dielectric. The effect of the negligible amounts of impurities on the resistivity of semi-conductors may sometimes be much more pronounced.

Thus, the physical picture of polarization of a dielectric may be represented as a negligibly small displacement in space of a very large number of charged particles of matter and the physical picture of electrical conduction of a dielectric as a motion of a relatively small number of charged particles for relatively large distances.

The displacement of charged particles during polarization may be regarded as an elastic shift of charges. When the effect of the voltage applied to a dielectric is discontinued, the displaced charges may tend to return to their initial positions, which never happens in the phenomenon of electrical conduction.

While the conduction current exists so long as a direct voltage is applied to a dielectric, the displacement current (capacitative current) appears only when the direct voltage is applied or taken off or generally when the magnitude of the applied voltage is changed. A capacitative current can exist in a dielectric for a long time only under the action of an alternating voltage. In the presence of a sinusoidal

alternating voltage the conduction current coincides in phase with the voltage, while the displacement current (in a linear dielectric) being also sinusoidal, is a quarter of a period ahead of the voltage.

TSC spectra^{292,293} are very useful to understand the processes of polarization and throw light on conduction mechanisms. Electrical conduction in polymers is governed by trapping levels²⁹⁴. Much can be learnt about traps with the help of TSC spectra. Photoelectric polarization of polymers also manifests trapping mechanisms²⁹⁵ and so much knowledge about traps is obtained by studying the photodepolarization currents.

Current voltage characteristics of PVAc films exhibited the lack of electrode effect but pronounced electrode effects were observed on TSC spectra and photodepolarization currents. These results show that the metal electrode is an important source of charge carriers which are atleast partly responsible for conduction and polarization of PVAc. Several investigators^{158,249} have suggested that the photoconduction in polymers involve carrier injection from electrodes. The surface states²⁴⁹ are one of the factors which affect the injection phenomena. The surface property of polymers seems so complex that it is not unreasonable to consider the existence of surface states. Suppose an insulator has a relatively large energy gap 6-8 eV with its Fermi level located above the mid gap and there is no surface state, then after contact with a

metal surface the electron transfer at contact equalize both fermi levels. The barrier height depends on the relative values of metal work function and electron affinity of insulator. This, however, can be completely changed if there are surface states at interface between the metal and the insulator. If these states are donor like and located between conduction band and fermi level then after contact these states tend to bend the band edge towards the fermi level, to make the electron injection from the metal electrode much easier, and under such a condition the electron injection should be enhanced.

On the other hand, if the surface states are acceptor like and located between valence band and fermi level then these states will act as stepping stone for the electrons to be injected from the valence band of the insulator to the metal and under such a condition the hole injection should be enhanced. Although these are the extreme cases, yet it seems possible that the injection current is affected by the surface levels like these.

The mechanism responsible for the formation of surface states has not been understood yet. But it is not unreasonable that the surface condition of PVAc samples before contacting of the metal electrode on them, the interaction of this surface condition with the metal and also the absorption of air can control the energy level, the nature and the density of surface states formed at the interface. Activation energy of PVAc was calculated by temperature variation of conductivity.

initial rise method of TSC and dielectric loss measurement. Trap depth was also calculated from photodepolarization current investigation. All the values are quite different from one another and help to propose the surface states.

Frequency and temperature dependence of dielectric loss of PVAc exhibited a loss maxima above the glass transition temperature of the polymer. TSC spectra of PVAc exhibited two current maxima, one at 45°C and the other round about 100°C. TSC peak arising at 45°C was absorbed completely when PVAc film was poled at higher temperatures or by larger electric fields. These results suggest that there are two processes of polarization, namely β and α . The β -relaxation process, accompanied with small activation energy, is due to the rotational motion of the long flexible side groups. This relaxation process could not be detected by dielectric loss method in audio frequency range. The α -relaxation having large activation energy, can be associated with a change of the dipolar orientation due to the segmental rotations or translations of the main chain. Two relaxation processes in the bulk PVAc have been observed by Yamafuji²⁷⁹ also. Besides these processes of polarization, space charge polarization due to injection of charge carriers from electrodes is also responsible for observed polarization in PVAc films.

Incorporation of iodine in PVAc exhibited marked changes in conductivity, dielectric loss, TSC spectra and photodepolarization currents, conductivity of PVAc is enhanced

greatly due to impregnation of the matrix with iodine. Increased conductivity results in enhanced dielectric losses. The increase in conductivity is attributed to the increase in mobility of charge carriers. Enhanced carrier mobility helps the doped film to collect more thermoelectric and photoelectric polarization.

Doping of halogens in polymers is known to form CT complexes. Formation of CT complexes has an effect of enhancing the conductivity of the polymer film. According to Swann⁸⁰, the mechanisms involved in the formation of CT complexes are :

- (1) Electron may go back to the polymer molecule from which it originates.
- (2) The electron may be retained by iodine and may move as a stable negative ion.
- (3) The electron may transfer from the negative iodine ion to another polymer molecule without motion of iodine molecule.
- (4) A charge exchange may occur between the negative iodine ion and a neutral iodine.

However, it is not possible to find out the exact mechanism responsible for formation of CT complexes in PVAc - iodine system with the present investigations.

CHAPTER VIII

Ram Adhar Shiv Adhar Stores

SUMMARY AND CONCLUSION

B.1 PVAc films were grown by isothermal immersion technique on cleaned Al substrates. To study the electrode effects films were also grown on Pb, Cu, Sn and Mo substrates. Laid on electrode assembly was used for the investigation. Iodine, an electron acceptor type impurity, was mixed in the polymer to understand the role of impurities in electrical conduction and polarization of the polymer.

Conductivity study was performed by noting the transient behaviour of current, electrode effect, thickness dependence and temperature dependence of current voltage characteristics of PVAc films. Effect of doping was investigated by observing the dependence of conductivity on temperature and current-voltage-temperature characteristics. Transient behaviour of current and the absence of significant electrode effect on current-voltage characteristics indicate carrier hopping mechanism. The linearity of current with square root of voltage at high field values favour Poole-Frenkel mechanism of conduction in pure and doped PVAc films but the temperature dependence can not be interpreted according to this mechanism. Conductivity of PVAc is greatly enhanced due to incorporation of iodine.

TSC spectra were investigated by varying the polarizing field, poling temperature, film thickness, electrode material and heating rate. Two relaxation processes namely β and α linked with the rotation of acetal groups and translation

of main polymer chain respectively are responsible for polarization of PVAc films. Space charge formation due to carriers injected from electrodes also plays a part here. Incorporation of iodine enhances TSC peaks and enables the polymer to store more charge.

Photodepolarization currents were measured by varying the polarizing field, time of polarization and electrode material. The carriers responsible for photopolarization are generated via exciton formation. This view is supported by pronounced electrode effect observed in photodepolarization of PVAc films. Due to doping of the polymer with iodine, new trapping sites are created and so the doped films store more polarization.

Dielectric behaviour of pure and iodine doped PVAc films was investigated by studying the dependence of capacitance on frequency and temperature and measuring the loss tangent. Dipole polarization involving ionic motion is prominent in PVAc. Addition of iodine reduces the viscosity of the polymer shifting α -relaxation peak to lower temperature. Doping also causes conduction losses.

It may be inferred from what has been mentioned above that besides dipole polarization, space charge polarization due to carrier injection from electrodes is responsible for observed polarization of PVAc films. Polarization effects influence the conduction mechanism in PVAc. Incorporation of iodine in the matrix improves the electret forming characteristics of PVAc films.

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